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Mitigation of nitrous oxide emissions by 3,4-dimethylpyrazole phosphate and 3,4-dimethylpyrazole succinic acid with reduced fertilizer application time while maintaining cabbage yield in Andosol fields

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ABSTRACT

Previous studies have reported that nitrification inhibitors are effective in reducing nitrous oxide emissions. However, no studies have reported the effectiveness of 3,4-dimethylpyrazole phosphate, and 3,4-dimethylpyrazole succinic acid in Andosol fields. Thus, the effects of nitrification inhibitors—dicyandiamide, 3,4-dimethylpyrazole phosphate, and 3,4-dimethylpyrazole succinic acid—on cabbage yield, nitrogen use efficiency, soil inorganic nitrogen, nitrous oxide emissions, and methane uptake were investigated in Andosol fields for six crop seasons over three years. The results showed that dicyandiamide inhibited nitrification only at temperatures lower than about 20°C and under relatively dry conditions but not at higher temperatures or under high rainfall. In contrast, 3,4-dimethylpyrazole phosphate and 3,4-dimethylpyrazole succinic acid effectively inhibited nitrification for all crop seasons. 3,4-dimethylpyrazole phosphate and 3,4-dimethylpyrazole succinic acid were effective in reducing nitrous oxide emissions ($P < 0.05$), but not dicyandiamide. Nitrification inhibitor application did not affect methane uptake by soil. Even though nitrification inhibitor applications did not increase the cabbage yield or nitrogen use efficiency, they could reduce the fertilizer application time (i.e., two fertilizer application times for urea vs only one basal fertilizer application time for nitrification inhibitor treatments). Additionally, 3,4-dimethylpyrazole phosphate and 3,4-dimethylpyrazole succinic acid maintained the yield even at a low nitrification inhibitor rate (0.5 % of applied nitrogen). Moreover, the former maintained yield at even a low nitrogen rate (175 kg N ha^{-1}, 70 % of the local standard application rate of 250 kg N ha^{-1}). Our results demonstrated that the nitrification inhibitors were effectively reduced the fertilizer application time, thus saving labor costs. Particularly, 3,4-dimethylpyrazole phosphate could reduce the nitrogen rate by 30 % compared to conventional nitrogen rates. These results suggested that 3,4-dimethylpyrazole phosphate and 3,4-dimethylpyrazole succinic acid application can be an effective way to ensure yield and reduce nitrous oxide emissions while saving labor costs.

1. Introduction

The global use of nitrogen (N) fertilizer is expected to increase to meet the growing demand for food and biofuel (Vishwakarma et al., 2022); however, it also causes nitrate (NO_3^-) leaching and nitrous oxide (N_2O) emissions. Agriculture is the largest source of N_2O, accounting for 51 % of anthropogenic emissions (Forster et al., 2021). Cabbage is an important vegetable crop worldwide, with an annual world production of about 74 million tons of fresh heads from 2.4 million ha in 2023 (FAOSTAT, 2025). Cabbage is also the most widely produced vegetable in Japan, with an annual production of about 1.4 million tons of fresh heads from 33,800 ha in 2023 (FAOSTAT, 2025). The fertilizer requirements for cabbage are high; local standard N application rate is 250 kg N ha^{-1} (Ibaraki Prefecture, 2022). However, only about half of the N applied to soil is used by crops, resulting in environmental pollution (Lassaletta et al., 2014).

Nitrification inhibitors can delay ammonia oxidation (first step of nitrification) in the soil and were developed to increase the N use efficiency of crops (Zerulla et al., 2001). According to global meta-analyses, nitrification inhibitors improve crop yield (Xia et al., 2017; Ma et al.,

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2023) and N use efficiency (Abalos et al., 2014; Xia et al., 2017), decrease NO_3^- leaching (Wang et al., 2025), and reduce N_2O emissions by 38–40 % (Akiyama et al., 2010; Ma et al., 2023). Dicyandiamide (DCD) and 3,4-dimethylpyrazole phosphate (DMPP) are the most used nitrification inhibitors worldwide (Zhang et al., 2024). However, the efficiency of DCD is relatively low; thus, high application rates (10 %–15 % DCD of applied N) are required for sufficient nitrification inhibition (Zerulla et al., 2001). Additionally, DCD is highly water soluble; it will be translocated within the soil profile by heavy rainfall, leading to the spatial separation of the nitrification inhibitor from the ammonium (NH_4^+) (Zerulla et al., 2001). In contrast, 3,4-dimethylpyrazole phosphate (DMPP) can inhibit nitrification with concentrations as low as 1 % of applied N (Zerulla et al., 2001). DMPP is not translocated within the soil profile; the spatial separation of the nitrification inhibitor from the fertilizer NH_4^+ should be minimal (Zerulla et al., 2001). Pasda et al. (2001) reported that DMPP increased the yield of various crops, especially at sites with a high precipitation rate, intensive irrigation, or light sandy soil. 3,4-dimethylpyrazole succinic acid (DMPSA) is a recently developed nitrification inhibitor. It is stable under basic conditions and can be combined with a wider range of fertilizers, including calcium ammonium nitrate or diammonium phosphate, which are not compatible with DMPP (Huérfano et al., 2016).

Some meta-analyses reported that nitrification inhibitors are effective in reducing N_2O emissions. For example, DCD and DMPP reduced N_2O emissions by 30 % and 50 % (Akiyama et al., 2010) and by 44 % and 47 % (Yang et al., 2016) globally compared with conventional fertilizers, respectively. Additionally, a meta-analysis in China reported that DCD and DMPP reduced N_2O emissions by 30 % and 60 %, respectively (Gao et al., 2021). A recent global meta-analysis found that DMPSA was the most effective nitrification inhibitor in reducing N_2O emissions (51 %), whereas the reduction rates of DCD and DMPP were 49 % and 38 %, respectively, although the number of available data for DMPSA was smaller than for other nitrification inhibitors (Ma et al., 2023).

Aerobic soil is a methane (CH_4) sink, accounting for 5 % of the global CH_4 sink (Forster et al., 2021). Ammonia-oxidizing bacteria (AOB) can also oxidize CH_4, whereas methane oxidizers can oxidize NH_4^+ (Bodelier and Steenbergh, 2014). Ammonium monooxygenase (AMO) and methane monooxygenase (MMO) are closely related. Thus, suppressing ammonia oxidation through nitrification inhibitor application might affect CH_4 oxidation in soil (Weiske et al., 2001).

DCD is the most widely used nitrification inhibitor in Japan, although its high solubility would lead to low effectiveness in inhibiting nitrification and NO_3^- leaching in the Asian Monsoon climates with high rainfall. Although DMPP has been used for about 20 years, mainly in Europe, it has become commercially available in Japan only recently (Tabuchi and Kobayashi, 2019); thus, it was not well studied in Japan, where Andosols share 47 % of upland fields (National Agriculture and Food Reasearch Organization, 2024). Andosols are volcanic soils characterized by low bulk density, good drainage, and high total C content (National Agriculture and Food Reasearch Organization, 2024). Tabuchi and Kobayashi (2019) reported that DMPP (1 % of urea-N) was less effective in inhibiting nitrification than DCD (10 % of urea-N) in Andosol in a soil incubation experiment, although the effectiveness of these nitrification inhibitors would change in the Andosol field conditions with high rainfall and good drainage. However, no study has reported the effectiveness of DMPP in Andosol fields. DMPSA is not commercially available in Japan so far, and its effectiveness in Andosols has not been reported either. Moreover, to our knowledge, no study has compared the effects of these nitrification inhibitors on crop yield, N use efficiency, and greenhouse gas emissions under Andosol field conditions; thus, an integrated assessment of the trade-offs between yield, N use efficiency, and greenhouse gas emissions is needed. This study aims to investigate the effects of three nitrification inhibitors—DCD, DMPP, and DMPSA—on cabbage yield, N use efficiency, soil inorganic N, and N_2O and CH_4 fluxes using automated gas sampling systems in Andosol fields. To this end, the following hypotheses were examined.

(1) The effectiveness of DCD in inhibiting nitrification is lower than that of DMPP and DMPSA in Andosol fields, especially when high rainfall is observed after fertilizer application.

(2) Nitrification inhibitors increase cabbage yield and N use efficiency.

(3) Nitrification inhibitors reduce N_2O emissions, but their effectiveness differs among inhibitors.

(4) Nitrification inhibitors affect CH_4 uptake by soil.

2. Material and methods

2.1. Field experiment settings

The experimental fields (A and B) were located at the Institute for Agro-Environmental Sciences, National Agriculture and Food Research Organization (NARO), Tsukuba, Japan (36°02'N, 140°11'E). The mean annual precipitation was 1326 mm, and the mean annual temperature was 14.3°C (1991–2020). The soil type of both fields was Silandic Andosol in the WRB classification, and the soil properties are displayed in Table S1. Cabbage (*Brassica oleracea*) was cultivated twice a year (spring and autumn) in Field A (2018) and adjacent Field B (2019 and 2020) (Table S2). Fields A and B were about 400 m apart. Both fields lie on upland and have good drainage with low bulk density (0.59–0.60).

The N fertilizer treatments in 2018 were zero-N control (Zero-N), 250 kg N ha^{-1} of urea (U-100, local standard treatment), 250 kg N ha^{-1} of urea with 10 % of DCD (DCD-100), 175 kg N ha^{-1} of urea with 0.5 % of DMPP (DMPP-L-70), 250 kg N ha^{-1} of urea with 0.5 % DMPP (DMPP-L-100), 175 kg N ha^{-1} of urea with 1 % of DMPP (DMPP-H-70), and 250 kg N ha^{-1} of urea with 1 % of DMPP (DMPP-H-100). The N fertilizer treatments in 2019 and 2020 were zero-N control (Zero-N), 250 kg N ha^{-1} of urea (U-100), 250 kg N ha^{-1} of urea with 10 % of DCD (DCD-100), 175 kg N ha^{-1} of urea with 0.5 % of DMPP (DMPP-L-70), 250 kg N ha^{-1} of urea with 0.5 % of DMPP (DMPP-L-100), 250 kg N ha^{-1} of urea with 1 % of DMPP (DMPP-H-100), 250 kg N ha^{-1} of urea with 0.5 % of DMPSA (DMPSA-L-100), and 250 kg N ha^{-1} of urea with 1 % of DMPSA (DMPSA-H-100) in 2019. The N treatments are detailed in Table 1. Superphosphate (250 kg P_2O_5 ha^{-1}) and potassium chloride (250 kg K_2O ha^{-1}) were applied as basal fertilizers in each crop season for all plots. Dolomite lime (1600 kg ha^{-1}) was applied in all plots approximately one month before the application of basal fertilizer. The basal fertilizer was broadcast and incorporated into a depth of approximately 15 cm by a rotary tiller. For U-100, basal N and additional N fertilizers were applied, following the local standard application rate and timing (200 kg N ha^{-1} as the basal fertilizer, and 50 kg N ha^{-1} as the additional fertilizer at 4–6 weeks after planting). Cabbage seedlings were transplanted just after the application of basal fertilizer on the same day. An additional N fertilizer was broadcasted to the surface of the soil. For nitrification inhibitor treatments, all fertilizers were applied as basal fertilizers (i.e., no additional fertilizer was applied). Cabbage heads were harvested two to three months after transplantation. After harvest, the outer leaves of cabbage were left on the surface of the soil in 2018, whereas they were roughly removed in 2019 and 2020. No irrigation was applied. All treatments were performed in triplicate. Plot sizes were 6 × 4 m in Field A and 6 × 3.5 m in Field B.

2.2. Sampling and analysis of plant and soil

For yield measurement, aboveground cabbage in 3 m^3 (10 plants) was collected from each plot at harvest. Fresh samples of the cabbage head and outer leaf were weighed. For dry weight measurements, head and outer leaf cabbage samples were dried at 70°C for two weeks. The carbon (C) and N contents of the dried samples were analyzed using an NC analyzer (SUMIGRAPH NC-22F, Sumika Chemical Analysis Service, Osaka, Japan). The N use efficiency was calculated as follows:

N use efficiency (%) = (aboveground plant N in fertilized treatment - aboveground plant N in Zero-N)/(applied N)× 100.

Table 1
N fertilizer treatments.

Year	Treatments	Total N application rate (kg N ha^{-1})	Basal N fertilizer application rate# (kg N ha^{-1})	Additional N fertilizer application rate (kg N ha^{-1})	Description
2018	Zero-N	0	0	0	Zero-N control
	U−100*	250	200	50	Local standard N application rate of urea
	DCD−100*	250	250	0	Local standard N application rate of urea with 10 % of DCD
	DMPP-L−70	175	175	0	70 % of the local standard N application rate of urea with 0.5 % of DMPP
	DMPP-L−100*	250	250	0	Local standard application rate of urea with 0.5 % of DMPP
	DMPP-H−70*	175	175	0	70 % of the local standard application rate of urea with 1 % of DMPP
	DMPP-H−100*	250	250	0	Local standard application rate of urea with 1 % of DMPP
2019 and 2020	Zero-N	0	0	0	Zero-N control
	U−100*	250	200	50	Local standard fertilizer application rate of urea
	DCD−100*	250	250	0	Local standard application rate of urea with 10 % of DCD
	DMPP-L−70	175	175	0	70 % of the local standard application rate of urea with 0.5 % of DMPP
	DMPP-L−100	250	250	0	Local standard application rate of urea with 0.5 % of DMPP
	DMPP-H−100*	250	250	0	Local standard application rate of urea with 1 % of DMPP
	DMPSA-L−100*	250	250	0	Local standard application rate of urea with 0.5 % of DMPSA
	DMPSA-H−100*	250	250	0	Local standard application rate of urea with 1 % of DMPSA

For nitrification inhibitor treatments, all fertilizers were applied as basal fertilizers. For the U-100 treatment, 200 kg N ha^{-1} was applied as the basal fertilizer, and 50 kg N $ha^{-1}$was applied as the additional fertilizer (4–6 weeks after planting), as recommended in the local standard fertilizer application methods.
* N_2O and CH_4 fluxes were measured only under these treatments due to the limited number of auto-chambers.

Soil temperature (5 cm depth), air temperature, and precipitation data were obtained from the Meteorological Data Acquisition System in NARO, Tsukuba. The soil volumetric water content (0–10 cm depth) was measured with EC-5 sensors (ECH2O, METER, Group Inc., Pullman, WA, US). The average of the data from ten positions in the field was converted to the water-filled pore space (WFPS) using a soil porosity of 0.756 ± 0.010 (mean and 1σ) and a calibration curve for Andosols (Akiyama et al., 2014). The bulk density was determined by measuring 100-mL soil core samples collected from 0 to 5 cm depth at four points in the field at the beginning of the experiment.

Soil samples were collected at 0–10 cm depth, and 15 g fresh soil samples were extracted with 100 mL of a KCl solution (100 g KCl L^{-1}) within 24 h after soil sampling and stored in a freezer (−28°C) until analysis. The analysis was performed within 4 months after extraction. The copper–cadmium reduction and a diazotization method were used to analyze NO_3^- (US EPA, 1993b), and the indophenol blue method was used to analyze NH_4^+ (US EPA, 1993a) using a continuous-flow analyzer (QuAAtro, BL TEC, Osaka, Japan).

2.3. N_2O and CH_4 flux monitoring

N_2O and CH_4 fluxes were measured only under selected treatments due to the limited number of auto-chambers (Table 1). Gas samples were collected using automated sampling systems (Akiyama et al., 2009). The gas sampling system automatically collects gas samples in glass vials using a syringe pump connected to an automated static chamber installed in the field. The systems used 15 polycarbonate auto-chambers, each with a cross-sectional area of 8100 cm^2 (90 × 90 cm) and a height of 65 cm. Each chamber's lid was closed automatically for 60 min, and three gas samples (0, 30, and 60 min) were collected and injected into vacuumed glass vials. Sampling was performed from 16:00–17:00 to obtain the daily average flux, and the timing was adapted from a previous study of diel changes in the N_2O flux in a nearby field, whereas the diel change of the gas flux was similar to the temperature change (Akiyama and Tsuruta, 2003). The gas samples were collected every two days during the cabbage cultivation periods and every four days during the fallow periods.

The gas samples are transferred to a laboratory and N_2O and CH_4 concentrations were analyzed by gas chromatography (GC-2014, Shimadzu, Kyoto, Japan) using a headspace auto-sampler (AOC5000, Shimadzu). The gas chromatography system analyzes N_2O and CH_4 concentrations within 10 min using a single 1 mL injection of the sample gas. The gas chromatography columns for the analysis were described by Sudo (2009). N_2 was used as the carrier gas, and N_2O concentrations were determined using a Nickel-63 (^{63}Ni) electron-capture detector at 340°C, doped with 5 % CH_4 containing Ar gas. CH_4 concentrations were determined using a flame ionization detector at 250°C. Standard gases (0.3, 0.5, 1, and 5 ppm N_2O and 2 ppm CH_4) were analyzed before and after the daily analyses of the samples. The coefficients of variation for repeated analyses of the standard gas (N_2O, 0.5 ppm; CH_4, 2.01 ppm) were 0.48 % for N_2O and 1.13 % for CH_4 ($n = 40$ for each gas). The fluxes were calculated from the linear increase or decrease in the gas concentrations during the sampling period. The hourly fluxes of CH_4 (mg CH_4 m^{-2} h^{-1}) and N_2O (μg N m^{-2} h^{-1}) are calculated as follows:

$$Flux = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \times \rho \times \frac{273}{273 + T}$$

where ΔC/Δt is the concentration change over time (ppm-CH_4 or ppb-N_2O h^{-1}); V is chamber volume (m^3); A is chamber area (m^2); ρ is gas density (0.717 kg m^{-3} for CH_4 and 1.977 kg m^{-3} for N_2O at 0°C); and T is the mean air temperature inside the chamber (°C).

The detection limits of flux were ± 0.003 mg m^{-2} h^{-1} for N_2O and ± 0.006 mg m^{-2} h^{-1} for CH_4. Cumulative emissions were calculated by integrating the daily flux over the measurement period (Minamikawa et al., 2015).

2.4. Statistical analyses

The effects of fertilizer treatments on cabbage yield and N use efficiency each year were compared using a linear mixed model. A residual test was also performed. The N treatments were considered as a fixed effect, and the crop season (spring and autumn) was treated as a random effect and replicates were nested within the crop season. The effects of fertilizer treatments on cumulative N_2O emissions and CH_4 uptake each year were compared using ANOVA followed by Tukey's test. The overall effectiveness of each fertilizer treatment on cabbage yield, N use efficiency, and N_2O emissions was analyzed using a linear mixed model with three years of data. Treatment and season were treated as fixed effects, whereas the year was treated as a random effect and replicates were nested within the year. All statistical analyses were performed using SPSS version 27.0 (IBM Inc., Chicago, Illinois, USA).

3. Results

3.1. Cabbage yield and nitrogen use efficiency

In the 2018 experiment, the cabbage head, outer leaf, and aboveground fresh and dry weights and the aboveground N content of the N-applied treatments were significantly higher than those of nontreated treatments (Zero-N; $P < 0.001$). No significant difference was observed among the N-applied treatments (Table. S3). Additionally, the N use efficiency did not significantly differ among the N-applied treatments. While the aboveground fresh weight of the N-applied treatments was similar for the spring and autumn cabbage, the aboveground dry weight and N content of the N-applied treatments was lower for the autumn cabbage than for the spring cabbage; consequently, the N use efficiency of the autumn cabbage (22 %–31 %) became lower than that of the spring cabbage (63 %–83 %).

In the 2019 experiment, the cabbage head fresh ($P < 0.001$) and dry weight ($P < 0.001$), outer leaf fresh ($P < 0.01$) and dry weights ($P < 0.01$), aboveground fresh ($P < 0.01$) and dry weight ($P < 0.01$), and aboveground N content ($P < 0.01$) of the N-applied treatments were significantly higher than those of the Zero-N treatments, while no significant difference was observed among the N-applied treatments (Table S4). N use efficiency did not significantly differ among the N-applied treatments except for the higher N use efficiency in DMPP-L70 than that in DMPSA-H100 ($P < 0.05$). The cabbage head, outer leaf, aboveground fresh and dry weights, and aboveground N content of the N-applied treatments were lower for the autumn cabbage than for the spring cabbage; consequently, the N use efficiency of autumn cabbage (14 %–19 %) became lower than that of spring cabbage (28 %–40 %).

In the 2020 experiment, the outer leaf fresh and dry weights and the aboveground fresh weight did not significantly differ among the treatments (Table S5). The cabbage head fresh ($P < 0.001$) and dry weight ($P < 0.001$), aboveground dry weight ($P < 0.05$), and aboveground N content ($P < 0.05$) of the N-applied treatments were significantly higher than that of the Zero-N, while no significant difference was observed among the N-applied treatments. The aboveground fresh weight of N-applied treatments was significantly higher than that of Zero-N ($P < 0.05$), except U-100. The N use efficiency did not significantly differ either among the N treatments, while the N use efficiency of autumn cabbage (30 %–42 %) was lower than that of spring cabbage (47 %–74 %).

A linear mixed model using all data was performed to analyze the overall effectiveness of each treatment on cabbage yield and N use efficiency (Table 2). The results indicated that the cabbage head fresh ($P < 0.01$) and dry weights ($P < 0.01$), outer leaf dry weight ($P < 0.01$), aboveground fresh ($P < 0.05$) and dry weights ($P < 0.05$), and total N ($P < 0.01$) of the N-applied treatments were higher than those of Zero-N. However, the same parameters did not significantly differ among the N-applied treatments. The outer leaf fresh weight of DMPP-L-70 was significantly higher than that of Zero-N ($P < 0.05$). N use efficiency did not significantly differ among the N-applied treatments.

3.2. Soil inorganic nitrogen

After the spring basal fertilizer application in 2018, the NH_4^+-N concentration of U-100 peaked after four days and decreased with the NO_3^--N increase (Fig. 1). The NH_4^+-N concentration of the DCD and DMPP treatments remained higher than that of the U-100 until the additional fertilizer application on U-100. The NH_4^+-N concentration of the DCD and DMPP treatments decreased in 6 weeks, while that of U-100 decreased in 4 weeks. However, NO_3^--N and NH_4^+-N concentrations in U-100 and DCD-100 displayed similar seasonal patterns under the autumn fertilizer application when the soil temperature was higher (mean of 2 weeks from fertilizer application: 24.2°C) than under the spring basal fertilizer application (18.5°C). In contrast, the NH_4^+-N concentration of DMPP treatments remained higher than in U-100 and DCD-100 for 4–5 weeks, while it decreased in 10 days in U-100 and DCD-100. Among the DMPP treatments, the NH_4^+-N level in DMPP-L100 decreased in 4 weeks compared to 5 weeks in DMPP-H100.

After applying the spring basal fertilizer in 2019, the NH_4^+-N concentration of U-100 peaked in 1 week and decreased in 3 weeks, while that of the DCD, DMPP, and DMPSA treatments remained higher and decreased in 7 weeks (Fig. 2). After the autumn basal fertilizer application, the NH_4^+-N concentration of U-100 peaked after 3 days and decreased after 9 days, whereas that of the DCD, DMPP, and DMPSA treatments remained higher until additional fertilizer application to U-100. Particularly, the NH_4^+-N concentration of DMPP-H100 remained high for a longer period (5 weeks) than that of the other nitrification inhibitor treatments (4 weeks). However, the period was shorter in autumn (4–5 weeks) than in spring (7 weeks), probably due to the higher soil temperature in autumn than in spring (23.9 vs 14.5°C).

After applying the spring basal fertilizer in 2020, the NO_3^--N and NH_4^+-N concentrations of U-100, DCD-100, and DMPSA-L100 displayed similar seasonal patterns (Fig. 3). The reason for the lack of effect of these nitrification inhibitors was probably due to heavy rainfall (cumulative rainfall for 2 weeks from fertilizer application: 126.5 mm) compared with the previous two spring basal fertilizer applications (68 mm in 2018 and 29 mm in 2019), although the soil temperature (12.7°C) was lower than the previous two spring basal fertilizer applications (18.5 and 14.5°C). In contrast, the NH_4^+-N concentration of DMPSA-H100 and DMPP treatments remained higher than that of U-100 and decreased in 7 weeks, while that of U-100 decreased in 2 weeks. After the autumn basal fertilizer application, the NO_3^--N and NH_4^+-N concentrations of U-100 and DCD-100 exhibited similar seasonal patterns in higher soil temperature conditions (22.6°C). The NH_4^+-N concentration of the DMPP and DMPSA treatments was higher than that of the U-100 and DCD-100 from 1 week to 3 weeks after fertilizer application. However, NO_3^--N and NH_4^+-N concentrations in all treatments decreased after a heavy rainfall of 107.5 mm within 4 days (7–10 October) due to a typhoon.

3.3. Nitrous oxide emissions

In the 2018 spring cabbage cultivation period, the N_2O emissions of DCD-100, DMPP-L100, DMPP-H70, and DMPP-H100 were significantly lower than those of U-100 ($P < 0.001$) by 56 %, 75 %, 80 %, and 80 %, respectively (Fig. 4, Table S6). In the 2018 autumn cabbage cultivation period, the N_2O emissions of DMPP-L100, DMPP-H70, and DMPP-H100 were significantly lower by 77 %, 89 %, and 85 %, respectively, than those of U-100 ($P < 0.01$). In contrast, the N_2O emissions of DCD-100 did not significantly differ from those of U-100, while those of DCD-100 were significantly higher than those under DMPP treatments ($P < 0.01$). Additionally, large N_2O peaks were observed under all treatments after harvesting the spring cabbage, whereas all the cabbage outer leaves were left on the surface of the soil under high-temperature conditions. Consequently, the annual N_2O emissions of the 2018 experiment did not significantly differ among treatments.

In the 2019 spring cabbage cultivation period, the N_2O emissions of

Table 2
Results of the linear mixed model on cabbage yield and nitrogen use efficiency.

a) Cabbage head fresh weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	21,924	a* *	2796	16,388	27,460	6
U−100	42,193	b	2796	36,656	47,729	6
DCD−100	43,102	b	2796	37,565	48,638	6
DMPP-L70	41,705	b	2796	36,169	47,242	6
DMPP-H70	46,425	b	4494	37,527	55,323	2
DMPP-L100	43,843	b	2796	38,306	49,379	6
DMPP-H100	44,517	b	2796	38,980	50,053	6
DMPSA-L100	42,015	b	3304	35,474	48,556	4
DMPSA-H100	43,274	b	3304	36,733	49,814	4

b) Cabbage outer leaf fresh weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	34,057	a*	5512	14,470	53,645	6
U−100	41,746	a	5512	22,159	61,334	6
DCD−100	42,787	a	5518	23,215	62,359	6
DMPP-L70	43,194	b	5513	23,608	62,779	6
DMPP-H70	45,179	a	6277	28,091	62,268	2
DMPP-L100	42,886	a	5514	23,304	62,467	6
DMPP-H100	43,082	a	5512	23,494	62,669	6
DMPSA-L100	42,815	a	5718	24,299	61,331	4
DMPSA-H100	43,368	a	5718	24,852	61,884	4

c) Cabbage aboveground fresh weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	55,982	a* *	4745	46,588	65,375	6
U−100	83,939	b	4745	74,545	93,333	6
DCD−100	85,737	b	4745	76,343	95,131	6
DMPP-L70	84,934	b	4745	75,540	94,327	6
DMPP-H70	89,989	b	7085	75,962	104,017	2
DMPP-L100	86,746	b	4745	77,352	96,140	6
DMPP-H100	87,598	b	4745	78,204	96,992	6
DMPSA-L100	85,636	b	5425	74,895	96,377	4
DMPSA-H100	87,550	b	5425	76,808	98,291	4

d) Cabbage head dry weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	1238	a* *	140	960	1516	6
U−100	2301	b	140	2023	2579	6
DCD−100	2355	b	140	2077	2633	6
DMPP-L70	2269	b	140	1991	2547	6
DMPP-H70	2452	b	212	2032	2871	2
DMPP-L100	2388	b	140	2110	2666	6
DMPP-H100	2417	b	140	2139	2695	6
DMPSA-L100	2347	b	161	2028	2666	4
DMPSA-H100	2428	b	161	2108	2747	4

e) Cabbage outer leaf dry weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	2478	a*	363	1115	3840	6
U−100	3061	b	363	1698	4424	6
DCD−100	3161	b	364	1804	4518	6
DMPP-L70	3153	b	363	1791	4515	6
DMPP-H70	3322	b	394	2119	4525	2
DMPP-L100	3133	b	364	1772	4494	6
DMPP-H100	3146	b	363	1783	4509	6
DMPSA-L100	3156	b	372	1853	4459	4
DMPSA-H100	3169	b	372	1866	4471	4

f) Cabbage aboveground dry weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	3716	a* *	456	2184	5249	6

(continued on next page)

Table 2 (*continued*)

f) Cabbage aboveground dry weight (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
U−100	5362	b	456	3829	6894	6
DCD−100	5490	b	457	3958	7022	6
DMPP-L70	5425	b	456	3893	6957	6
DMPP-H70	5762	b	541	4398	7126	2
DMPP-L100	5519	b	457	3986	7051	6
DMPP-H100	5563	b	456	4030	7095	6
DMPSA-L100	5521	b	479	4076	6966	4
DMPSA-H100	5624	b	479	4178	7069	4

g) Cabbage total N (kg ha^{-1})

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
Zero-N	83	a* *	17	24	141	6
U−100	169	b	17	110	228	6
DCD−100	177	b	17	119	236	6
DMPP-L70	162	b	17	104	221	6
DMPP-H70	183	b	19	132	235	2
DMPP-L100	167	b	17	108	225	6
DMPP-H100	173	b	17	115	232	6
DMPSA-L100	174	b	17	118	229	4
DMPSA-H100	170	b	17	115	226	4

h) Nitrogen use efficiency (%)

Treatment	Estimate		SE	95 % CI		Number of crop seasons
				Low	High	
U−100	34	a*	7.7	7	61	6
DCD−100	39	a	7.7	12	66	6
DMPP-L70	45	a	7.7	19	72	6
DMPP-H70	37	a	8.4	13	61	2
DMPP-L100	40	a	7.7	13	67	6
DMPP-H100	36	a	7.7	9	63	6
DMPSA-L100	37	a	7.9	11	63	4
DMPSA-H100	36	a	7.9	10	62	4

* *Different letters represent significant differences in the linear mixed model ($P < 0.01$).
Treatment and season were considered fixed effects, while the year and replicates were treated as a random effect.
*Different letters represent significant differences in the linear mixed model ($P < 0.05$).

DMPP-H100 were significantly lower by 54 % than those of U-100 (Fig. 5, Table S7; $P < 0.05$). The N_2O emissions of DCD-100, DMPSA-L100, and DMPSA-H100 were also lower than those of U-100, but not significantly. In the 2019 autumn cabbage cultivation period, the N_2O emissions of DMPP-100, DMPSA-L100, and DMPSA-H100 were significantly lower by 85 %, 83 %, and 69 %, respectively, than those of U-100 ($P < 0.05$), while those of DCD-100 did not significantly differ from those of U-100. In the 2019 experiment, the cabbage's outer leaves were roughly removed from the soil surface by hand but could not be removed completely. Consequently, smaller N_2O peaks were observed compared to 2018 under all treatments after harvesting the spring cabbage. In the 2019 experiment, the annual N_2O emissions of DMPP-H100 and DMPSA-L100 were significantly lower by 57 % and 60 %, respectively, than those of U-100 ($P < 0.05$). The annual N_2O emissions in DMPSA-H100 and DCD-100 were also lower than those of U-100 but not significantly different.

In the 2020 spring cabbage cultivation period, the N_2O emissions of DCD-100, DMPP-H100, DMPSA-L100, and DMPSA-H100 were significantly lower by 56 %, 91 %, 69 %, and 82 %, respectively, than those of U-100 (Fig. 6, Table S8; $P < 0.05$). During the autumn cabbage cultivation period, the N_2O emissions of DMPP-H100 and DMPSA-L100 were significantly lower by 70 % and 68 %, respectively, than those of U-100 ($P < 0.05$), while the N_2O emissions of DCD-100 and DMPSA-H100 were lower but not significantly different from those of U-100. Similar to the 2019 experiment, the cabbage's outer leaves were roughly removed after the harvest, and smaller N_2O peaks than those in 2018 were observed under all treatments after harvesting the spring cabbage. In 2020, the annual N_2O emissions of DCD-100, DMPP-H100, DMPSA-L100, and DMPSA-H100 were significantly lower by 46 %, 88 %, 66 %, and 75 %, respectively, than those of U-100 ($P < 0.05$). Additionally, the annual N_2O emissions of DMPP-H100 were significantly lower than those of DCD-100 in 2020.

A linear mixed model was used to analyze the overall effectiveness of each treatment on N_2O emissions (Table 3). The result of the linear mixed model revealed that the N_2O emissions of DMPP-H100 and DMPSA-H100 during the cabbage growing period were significantly lower by 81 % and by 70 %, respectively, compared to those of U-100 ($P < 0.05$), while those under other nitrification inhibitor treatments were lower but not significantly. During the period after harvesting the cabbage (N_2O emissions from crop residue), the N_2O emissions of the nitrification inhibitor-applied treatments did not significantly differ from those of U-100. The annual N_2O emissions of DMPP-H100, DMPSA-L100, and DMPSA-H100 were significantly lower by 67 %, 60 %, and 62 % than those of U-100, respectively ($P < 0.05$).

3.4. *Methane uptake*

CH_4 uptake by the soil was observed in all treatments for all 3 years (Table S9–11, Fig S1), and the amount was similar (−2.54 to −1.25 kg C ha^{-1}) over the 3 years. No significant difference was observed among the N- applied treatments at any period, suggesting that DCD, DMPP, and DMPSA applications did not affect the CH_4 uptake.

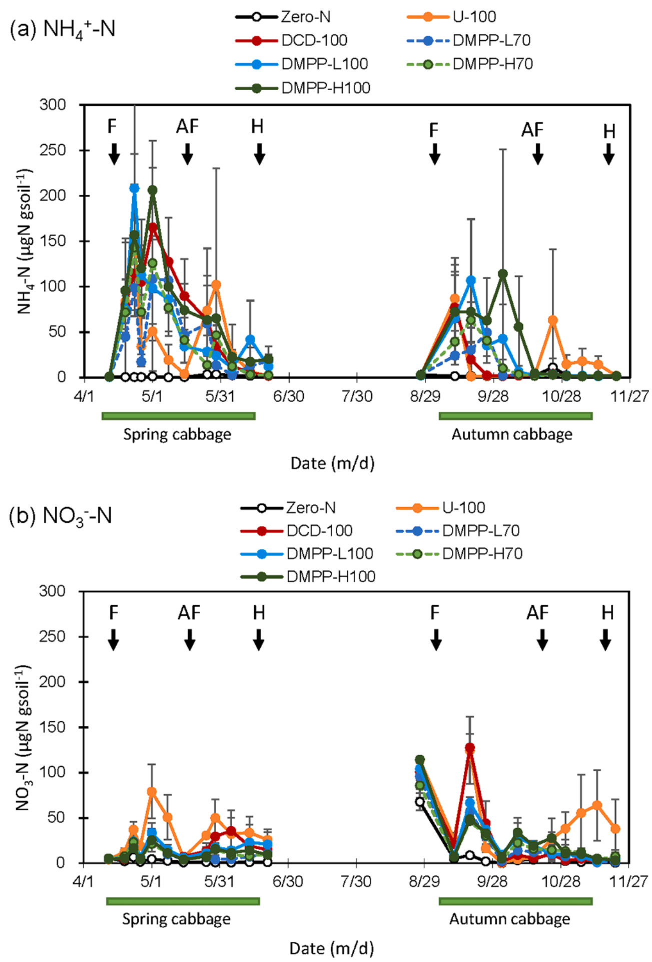

Fig. 1. Seasonal change in soil inorganic nitrogen in 2018. (a) NH_4^+-N, (b) NO_3^--N. BF, basal fertilizer application; AF, additional fertilizer application for U-100. No additional fertilizer was applied to the DCD and DMPP treatments. H, harvest.

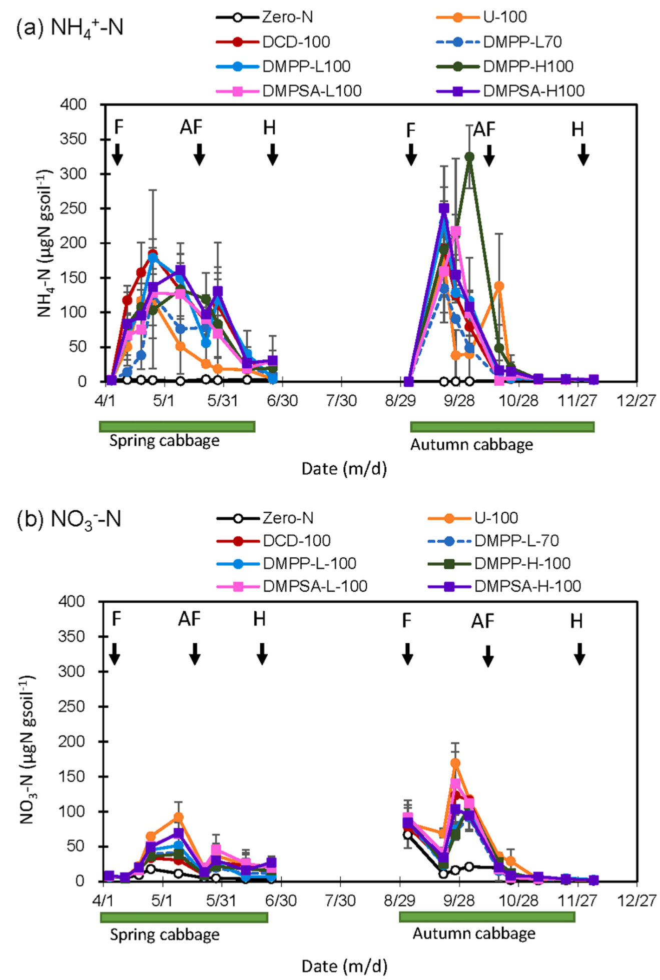

Fig. 2. Seasonal change in soil inorganic nitrogen in 2019. (a) NH_4^+-N, (b) NO_3^--N. BF, basal fertilizer application; AF, additional fertilizer application for U-100. No additional fertilizer was applied to the DCD, DMPP and DMPSA treatments. H, harvest.

4. Discussions

4.1. Cabbage yield and nitrogen use efficiency

Cabbage head fresh and dry weights did not significantly differ among the N-applied treatments for each year (Table S3–S5). The result of the linear mixed model using all data also indicated that the cabbage head fresh and dry weights did not significantly differ among the N-applied treatments (Table 2). The fresh and dry cabbage yields under DMPP-L70 and DMPP-H70 did not significantly differ from that of U-100, suggesting that DMPP could maintain the yield at a low N application rate (70 % of conventional application rate) with a high (1 %) or low (0.5 % of applied N) DMPP rate.

A global meta-analysis revealed that DMPP increased the N use efficiency of various crops significantly by 12.9 % (n = 15), while yield increased by 7.5 % (n = 22) but not significantly (Abalos et al., 2014). Another meta-analysis reported that DMPP increased the yield of various crops by 6 % ($n = 14$), whereas DMPSA ($n = 3$) and DCD ($n = 15$) had no significant effect, although the number of available data was not enough, especially for DMPSA (Ma et al., 2023). A meta-analysis in China reported that nitrification inhibitor application significantly increased grain yield by 10.0 % and N use efficiency by 12.1 % (Xia et al., 2017). Pasda et al. (2001) reported that DMPP increased the yield of various crops, especially at sites with a high precipitation rate or intensive irrigation and light sandy soil. However, no significant yield increase was observed for cabbage under the Andosol fields in our study. Pasda et al. (2001) reported that DMPP application did not significantly increase lettuce yield, although yield increases were observed for most vegetable crops, whereas cabbage was not included in their study. Abalos et al. (2014) reported that the effect of nitrification inhibitors on yield showed much larger variation than those of cereals and forage, suggesting this was due to the inherent large intra-variability within the vegetable crops. Fewer studies have reported the effects of nitrification inhibitors on vegetable crops than on cereals and forage; thus, further studies are needed.

Even though the DCD, DMPP, and DMPSA applications did not increase the cabbage yield or N use efficiency, they could reduce the fertilizer application time (i.e., two fertilizer application times for U-100 vs only one for nitrification inhibitor treatments). Additionally, DMPP could maintain the yield even at a low nitrification inhibitor rate (0.5 % of applied N) and low N application rate (70 % of conventional application rate). Also, DMPSA could maintain the yield even at a low nitrification inhibitor rate (0.5 % of applied N). Our results revealed that DCD, DMPP, and DMPSA were effective in reducing the fertilizer application time, thus saving labor costs for additional fertilizer application. Particularly, DMPP could reduce the N fertilizer use by 30 % from the conventional N application rate.

4.2. Effectiveness of nitrification inhibitors

DCD inhibited nitrification during 2 weeks after two spring fertilizer

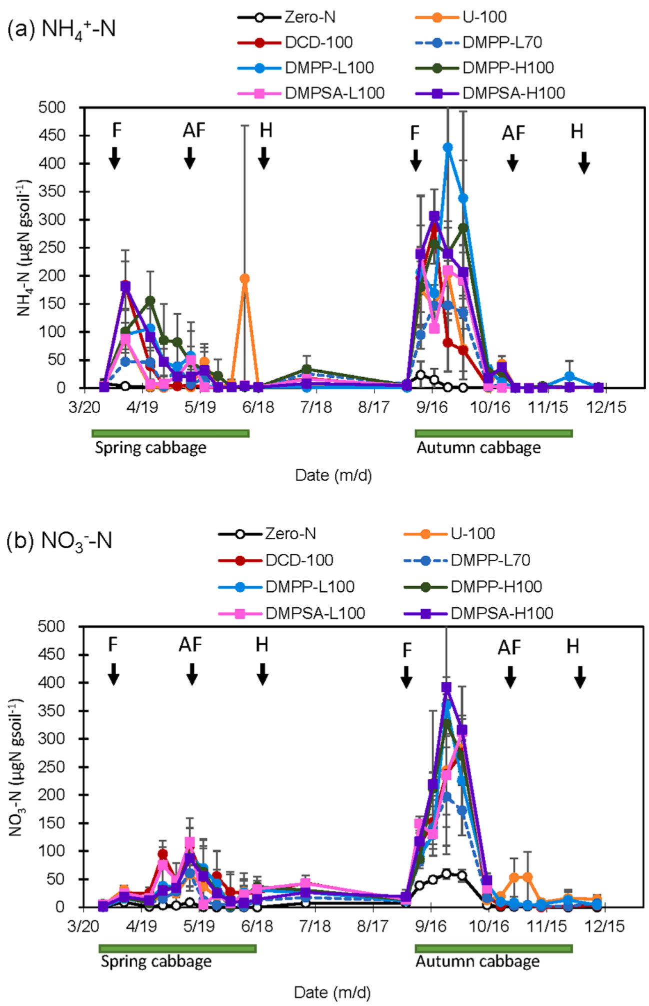

Fig. 3. Seasonal change in soil inorganic nitrogen in 2020. (a) NH_4^+-N, (b) NO_3^--N. BF, basal fertilizer application; AF, additional fertilizer application for U-100. No additional fertilizer was applied to the DCD, DMPP, and DMPSA treatments. H, harvest.

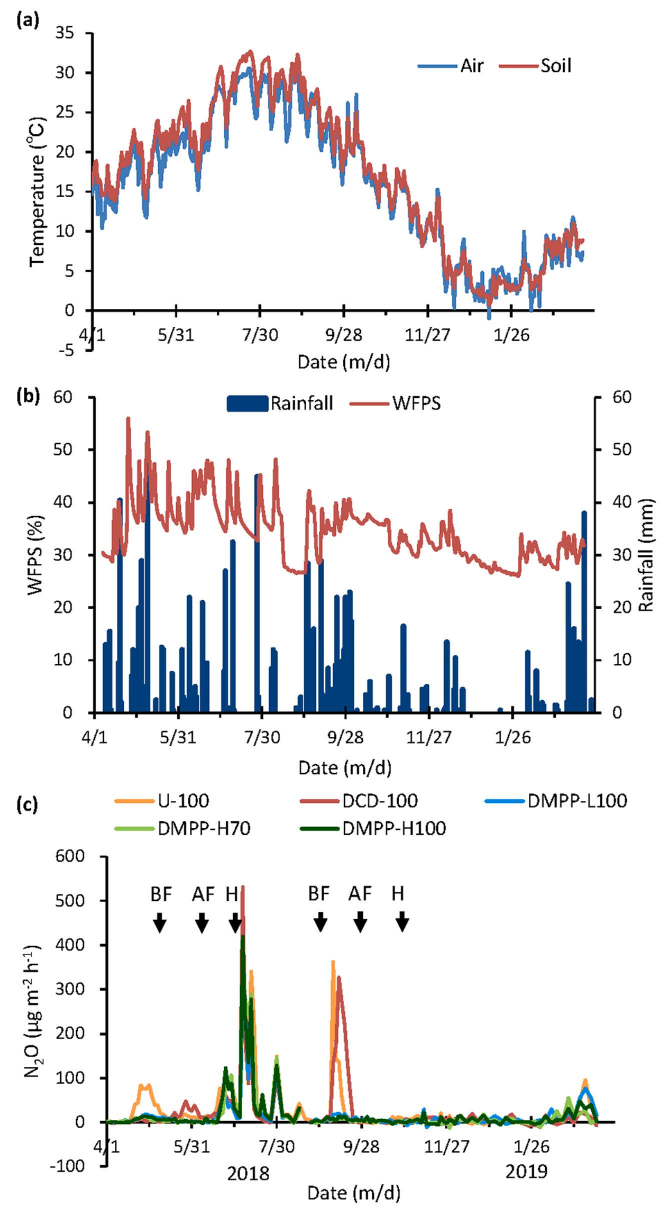

Fig. 4. Seasonal change in temperatures (a), rainfall and WFPS (b), and N_2O flux (c) in the 2018 experiment. BF, basal fertilizer application; AF, additional fertilizer application for U-100. No additional fertilizer was applied to the DCD and DMPP treatments. H, harvest.

applications in relatively lower soil temperatures (14.5–18.5°C) and low precipitation (29–68 mm), while it failed to inhibit nitrification under the three autumn fertilizer applications at higher temperatures (22.6–24.2°C) and one spring fertilizer application under high precipitation (126.5 mm) (Figs. 1, 2, and 3). A soil incubation study showed that the effectiveness of DCD on nitrification inhibition decreases with the increase in temperature (Kelliher et al., 2008). Raza et al. (2022) also reported that DCD degraded faster at high temperature (25°C) and moisture (60 % WFPS) than at low temperature (10°C) and moisture (40 % WFPS) in a soil incubation experiment and suggested that DCD is more suitable for regions with low temperature and low moisture. Additionally, Kelliher et al. (2014) reported that the DCD concentration decreased much faster under field conditions than in soil incubation experiments in the laboratory at the same temperature. Extrapolating the linear relationship between the mean soil temperature and the DCD half-life in New Zealand fields by Kelliher et al. (2014), the half-life of DCD was estimated at 22–31 days under spring fertilizer applications and 10–13 days under autumn fertilizer applications. In addition, DCD has high water solubility; DCD will translocate within the soil profile under heavy rainfall, leading to the spatial separation of the nitrification inhibitor from NH_4^+ (Zerulla et al., 2001). The shorter half-life period and higher water solubility should result in the failure of inhibition by DCD under autumn fertilizer applications. The high water solubility of DCD is particularly problematic in Japan with the high rainfall of the Asian Monsoon Climate, resulting in the low effectiveness of DCD in inhibiting nitrification.

In contrast to DCD, DMPP inhibited nitrification at low (0.5 % of N) and high (1 % of N) additional rates under all six fertilizer applications (i.e., low (12.7–18.5°C) and high (22.6–24.2°C) temperature conditions). The decomposition rate of DMPP and DCD increases with temperatures (Kelliher et al., 2014; Zerulla et al., 2001), and Guardia et al. (2017) reported a similar decomposition rate and inhibition for both nitrification inhibitors. However, DMPP was more effective in inhibiting nitrification at high temperatures in our study.

Tabuchi and Kobayashi (2019) also reported that DMPP (1 % of urea-N) was less effective in inhibiting nitrification than DCD (10 % of urea-N) in an Andosol incubation experiment at 25°C. However, our results demonstrated that DMPP was more effective in inhibiting nitrification in Andosol field conditions, probably because the higher solubility of DCD resulted in less inhibition while DMPP was not translocated within the soil profile, resulting in a minimal spatial

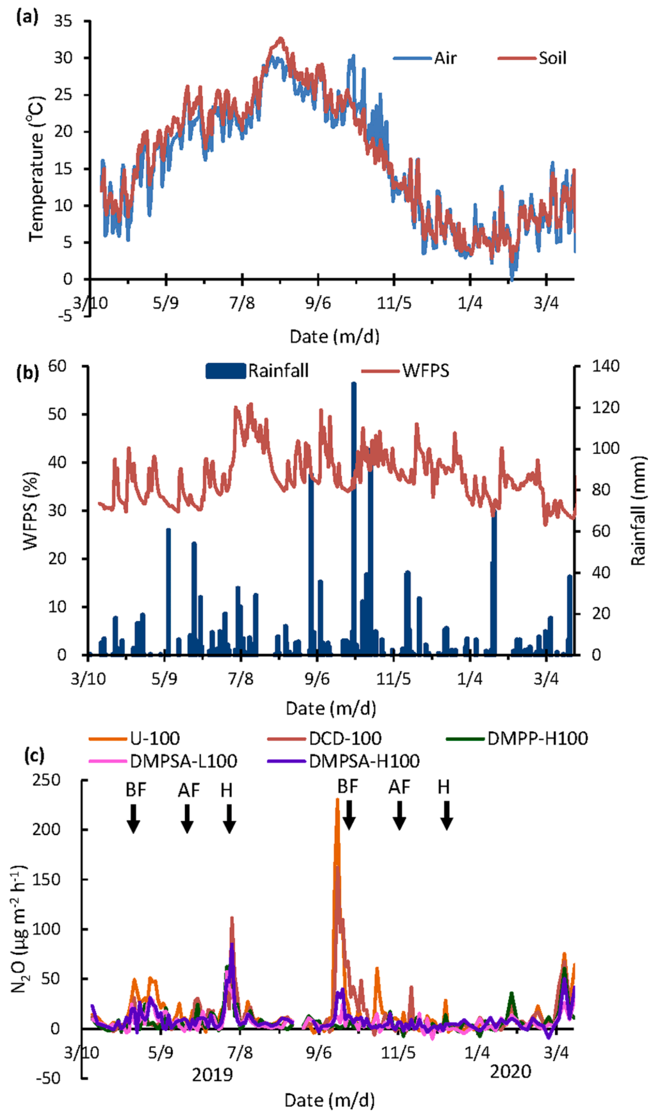

Fig. 5. Seasonal change in temperatures (a), rainfall and WFPS (b), and N_2O flux (c) in the 2019 experiment. BF, basal fertilizer application; AF, additional fertilizer application for U-100. No additional fertilizer was applied to the DCD, DMPP, and DMPSA treatments. H, harvest.

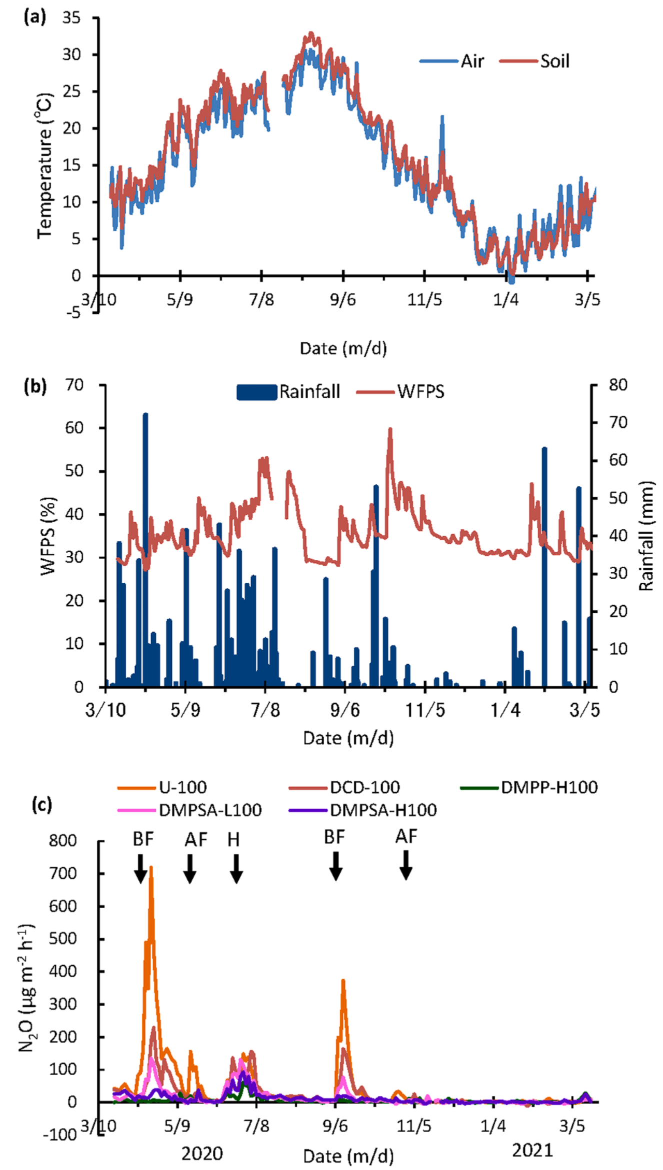

Fig. 6. Seasonal change in temperature (a), rainfall and WFPS (b), and N_2O flux (c) in the 2020 experiment. BF, basal fertilizer application; AF, additional fertilizer application for U-100. No additional fertilizer was applied to the DCD, DMPP, and DMPSA treatments. H, harvest.

separation of DMPP from the NH_4^+ fertilizer (Zerulla et al., 2001).

DMPSA at a high additional rate (1 % of N) inhibited all four fertilizer applications in Andosol fields. In contrast, DMPSA at a low additional rate (0.5 % of N) was effective under low (29–68 mm) but not high (126.5 mm) precipitations.

Note that nitrification inhibition was assessed by measuring soil NH_4^+ and NO_3^- -N concentrations in this study. While this approach is commonly used in field studies, it has limitations as it reflects the net effect of multiple nitrogen transformation processes, including plant uptake, leaching, and immobilization.

4.3. Nitrous oxide emissions

Coinciding with the effectiveness of DCD on the inhibition of nitrification, N_2O reduction by DCD was only observed under relatively low temperatures and dry conditions; the N_2O emissions of DCD-100 were significantly lower than those of U-100 under two spring cabbage cultivation periods and were lower, but not significantly, at one spring cultivation period (Table S6–8, Figs. 4–6). In contrast, the N_2O emissions of DCD-100 were similar or even higher than those of U-100 during the autumn cabbage periods with higher temperatures after fertilizer application (22.6–24.2°C) compared to the spring basal fertilizer application (12.7–17.5°C). DCD was effective for nitrification inhibition only at low temperatures (Figs. 1, 2, and 3); consequently, DCD reduced N_2O emissions at temperatures below approximately 20°C but not at higher temperatures. The result of the linear mixed model indicated that the N_2O emissions of DCD-100 during cultivation period and the annual emissions were lower than those of U-100 by 33 % and 32 %, respectively, but not significantly (Table 3). Because N_2O reduction by DCD was only observed under relatively low temperatures and dry conditions, its overall effectiveness on N_2O reduction became insignificant in contrast to DMPP and DMPSA. A global meta-analysis reported that DCD reduced N_2O emissions by 30 % compared to conventional fertilizers (Akiyama et al., 2010), a similar reduction reported in our study. Recent meta-analyses also reported that DCD reduced N_2O emissions by 19 % (Tufail et al., 2023) and 49 % (Ma et al., 2023).

In contrast to DCD, the N_2O reduction by DMPP application was stable even at high temperatures. The N_2O emissions of DMPP-L100 and

Table 3
Results of the linear mixed model on N_2O emissions.

a) N_2O emissions during the cabbage cultivation period (kg N ha^{-1})

Treatment	Estimate		SE	95 % CI		Reduction rate# (%)	Number of crop seasons
				Low	High		
U−100	0.71	a*	0.17	0.38	1.05	-	6
DCD−100	0.48	a	0.17	0.15	0.81	33	6
DMPP-H70	0.17	a	0.23	−0.28	0.62	76	2
DMPP-L100	0.21	a	0.23	−0.24	0.66	71	2
DMPP-H100	0.14	b	0.17	−0.19	0.47	81	6
DMPSA-L100	0.29	a	0.18	−0.07	0.66	59	4
DMPSA-H100	0.22	b	0.18	−0.15	0.58	70	4

b) N_2O emissions during the period after the cabbage harvest (from crop residue)

Treatment	Estimate		SE	95 % CI		Reduction rate# (%)	Number of crop seasons
				Low	High		
U−100	0.41	a	0.16	0.09	0.73	-	6
DCD−100	0.30	a	0.19	−0.02	0.62	26	6
DMPP-H70	0.37	a	0.19	−0.01	0.74	10	2
DMPP-L100	0.23	a	0.16	−0.15	0.60	44	2
DMPP-H100	0.27	a	0.17	−0.05	0.59	33	6
DMPSA-L100	0.20	a	0.17	−0.13	0.54	50	4
DMPSA-H100	0.25	a	0.16	−0.08	0.59	37	4

c) Annual N_2O emissions

Treatment	Estimate		SE	95 % CI		Reduction rate#	Number of
				Low	High	(%)	years
U−100	2.49	a*	0.34	1.80	3.17	-	6
DCD−100	1.69	a	0.34	1.00	2.38	32	6
DMPP-H70	1.25	a	0.48	0.27	2.23	50	2
DMPP-L100	1.05	a	0.48	0.07	2.03	58	2
DMPP-H100	0.83	b	0.34	0.14	1.52	67	6
DMPSA-L100	0.99	b	0.38	0.22	1.77	60	4
DMPSA-H100	0.94	b	0.38	0.17	1.71	62	4

*Different letters represent significant differences in the linear mixed model ($P < 0.05$). Treatment and season were considered fixed effects, while the year and replicates were treated as a random effect.
Reduction rate = (N_2O emissions from nitrification inhibitor treatments)/(N_2O emissions from U-100), expressed in %.

DMPP-H100 were significantly lower than those of U-100 at the two and all six cultivation periods, respectively, reflecting that DMPP inhibited nitrification under all fertilizer applications (Table S6–8, Figs. 4–6). The result of the linear mixed model revealed that the N_2O reduction rates of DMPP-L100 and DMPP-H100 during cultivation period were 71 % (not significant) and 81 % (significant, $P < 0.05$), respectively, compared to those of U-100 (Table 3). The annual emissions of DMPP-L100 and DMPP-H100 were also lower by 58 % (not significant) and 67 % (significant, $P < 0.05$) compared to U-100, respectively. These results showed that DMPP, especially at a 1 % addition rate, was effective in reducing N_2O emissions in Andosols even at relatively high temperatures or rainfall, while no study has reported the effectiveness of DMPP on N_2O emissions in Andosol fields to our knowledge. Guo et al. (2022) also reported that DMPP was a more effective nitrification inhibitor to reduce N_2O emissions, irrespective of soil moisture and temperature, while the effectiveness of DCD was largely affected by temperature and moisture in an incubation experiment. A meta-analysis reported that DMPP reduced N_2O emissions by 50 % compared with conventional fertilizers (Akiyama et al., 2010). Recent meta-analyses also reported that DMPP reduced N_2O emissions by 20 % (Tufail et al., 2023) and 38 % (Ma et al., 2023).

Although DMPSA treatments reduced N_2O emissions compared to U-100 in all four cultivation periods, statistical significance was not constantly observed. The N_2O emissions of DMPSA-L100 were significantly lower than those of U-100 in two autumn and one spring cultivation periods and were lower, but not significantly different, in another spring cultivation period. The N_2O emissions of DMPSA-H100 were lower than those of U-100 in one spring and one autumn cultivation period and were lower, but not significantly different, in other spring and autumn cultivation periods (Table S6–8, Figs. 4–6). The result of the linear mixed model revealed that the N_2O emissions of DMPSA-L100 and DMPSA-H100 during the cabbage cultivation period were lower by 59 % (not significant) and 70 % (significant, $P < 0.05$), respectively, compared to those of U-100 (Table 3). The annual emissions of DMPSA-L100 and DMPSA-H100 displayed a significant reduction by 60 % and 62 % compared to those of U-100, respectively. These results showed that DMPSA was effective in reducing N_2O emissions in Andosol fields, which has not been reported so far. A recent global meta-analysis found that DMPSA was the most effective nitrification inhibitor, reducing N_2O emissions by 50.7 % compared to conventional fertilizers, although the number of available data was smaller than for other nitrification inhibitors because it is relatively new (Ma et al., 2023).

After harvesting the spring cabbage, large N_2O peaks were observed in all treatments (Figs. 4–6), probably due to cabbage residue decomposition under high-temperature conditions; the peak was larger in 2018 when all the cabbage outer leaves were left on the surface of the soil compared with that of 2019 and 2020 when cabbage outer leaves were roughly removed. Similar N_2O peaks were observed after low C/N crop residue inputs, such as cabbage (C/N: 10–11) and potato (C/N: 11), in summer (Akiyama et al., 2020). Yamamoto et al., (2017) reported that the N_2O production process from potato residues was mainly denitrification based on the natural abundance of $^{15}N_2O$ site preference analysis. Nitrification inhibitors indirectly affect denitrification by reducing the NO_3^- concentration, which is the substrate for the denitrification processes. For example, Chaves et al. (2006) reported that DCD and DMPP inhibited the nitrification of NH_4^+ from cauliflower residue decomposition, whereas DMPP displayed longer inhibition in an incubation experiment. However, in this study, nitrification inhibitors were incorporated into the soil, while the N_2O production site probably was residue left on the surface of the soil rather than in the soil. Additionally, nitrification inhibitors were incorporated in the basal fertilizer application about two to three months before the harvest so that they were mostly degraded at the time of residue input. Because of the spatial and temporal separation of nitrification inhibitors and cabbage residue, nitrification inhibitor application at the basal fertilizer application would struggle to reduce N_2O emissions after residue input. The N_2O emissions under the nitrification inhibitor treatments after residue input were not significantly different from those of U-100 for all six seasons (Table S6–8). Additionally, the result of the linear mixed model indicated that the N_2O emissions under nitrification inhibitor treatments after residue input were not significantly different from those of U-100 (Table 3).

4.4. Mehane uptake

Aerobic soil is a CH_4 sink, accounting for 5 % of the global CH_4 sink (Forster et al., 2021). The annual CH_4 uptake in this study (−2.54 to −1.25 kg C ha^{-1}) was similar to that in previous studies on Andosol agricultural fields (Akiyama et al., 2014, 2015, 2020). AOB can oxidize NH_4^+ and CH_4, whereas methane oxidizers can oxidize CH_4 and NH_4^+ (Bodelier and Steenbergh, 2014). Akiyama et al. (2014) reported significant relationships between the ammonia oxidation potential, *amoA* abundances of AOB and AOA, and the CH_4 uptake in field measurements of different soil types, suggesting the importance of AOB and AOA in CH_4 oxidation in agricultural soils treated with N fertilizers. Wang et al. (2016) reported that the CH_4 uptake decreased with the increase in AOA *amoA* abundances, whereas it increased with the AOB *amoA* abundances, suggesting that AOB oxidizes CH_4 in N-enriched agricultural soil. Weiske et al. (2001) reported that DMPP stimulated CH_4 oxidation by 28 % compared with the control without DMPP, suggesting that suppressing the activity of AMO by nitrification inhibitors might facilitate the activity of MMO, thus the stimulation of CH_4 oxidation. However, DCD, DMPP, and DMPSA did not affect CH_4 fluxes compared to U-100 in this study (Table S9–11, Fig S1). Weiske et al. (2001) also reported no significant effect of DCD on CH_4 uptake by soil. In addition, DCD did not affect CH_4 uptake by soil in the Andosol and Fluvisol fields in the same region as in this study (Akiyama et al., 2015). A recent meta-analysis reported that DCD and DMPP did not affect CH_4 uptake by soil in general (Tufail et al., 2023). In a winter wheat field, DMPSA did not affect CH_4 uptake by soil (Corrochano-Monsalve et al., 2020).

5. Conclusions

Our results revealed that DMPP and DMPSA were effective in inhibiting nitrification at relatively high temperatures and rainfall in Andosol fields. However, DCD was effective in inhibiting nitrification only under about 20°C and dry conditions, but not at higher temperatures or rainfall. Moreover, DMPP and DMPSA were effective in reducing N_2O emissions in the Andosol fields. In contrast, the effectiveness of DCD in N_2O reduction was not significant. DCD, DMPP, and DMPSA applications did not affect the CH_4 uptake by the soil.

Even though DCD, DMPP, and DMPSA applications did not increase the cabbage yield or N use efficiency, they could reduce the fertilizer application time (i.e., two fertilizer application times for U-100 vs only one for nitrification inhibitor treatments). Additionally, DMPP maintained the yield even at a low nitrification inhibitor rate (0.5 % of applied N) and low N application rate (175 kg N; 70 % of conventional application rate). Moreover, DMPSA maintained the yield even at a low nitrification inhibitor rate (0.5 % of applied N). Our results demonstrated that DCD, DMPP, and DMPSA were effective in reducing the fertilizer application time, thus saving labor costs for additional fertilizer application. Particularly, DMPP could reduce the N rate by 30 % compared to conventional N rates. These results suggest that DMPP and DMPSA can be an effective way to ensure yield and reduce N_2O emissions while saving labor costs. Although our study showed the effectiveness of DMPP and DMPSA on the inhibition of nitrification and N_2O reduction in Andosol fields, further research on these nitrification inhibitors is needed using a variety of crops and soil types.

CRediT authorship contribution statement

Yong Wang: Writing – review & editing, Investigation. **Masahito Hayatsu:** Writing – review & editing, Investigation. **Hiroko Akiyama:** Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **Yuma Sasaki:** Writing – review & editing, Investigation. **Kanako Tago:** Writing – review & editing, Investigation.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hiroko Akiyama reports financial support was provided by BASF Japan Ltd. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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