


Article

Comparative Effectiveness of Four Nitrification Inhibitors for Mitigating Carbon Dioxide and Nitrous Oxide Emissions from Three Different Textured Soils

Yafei Guo, Asif Naeem and Karl H. Mühling * 

Institute of Plant Nutrition and Soil Science, Kiel University, Hermann-Rodewald-Strasse 2, 24118 Kiel, Germany; yguo@plantnutrition.uni-kiel.de (Y.G.); anaem@plantnutrition.uni-kiel.de (A.N.)

* Correspondence: khmuehling@plantnutrition.uni-kiel.de; Tel.: +49-(431)-880-3189

Abstract: Nitrification inhibitors (NIs) can be used to reduce both NO_3^- -N leaching and N_2O -N emissions. However, the comparative efficacies of NIs can be strongly affected by soil type. Therefore, the efficacies of four nitrification inhibitors (dicyandiamide (DCD), 3, 4-dimethylpyrazole phosphate (DMPP), nitrogenous mineral fertilizers containing the DMPP ammonium stabilizer (ENTEC) and active ingredients: 3.00–3.25% 1, 2, 4-triazole and 1.50–1.65% 3-methylpyrazole (PIADIN)) were investigated in three different textured N-fertilized ($0.5 \text{ g NH}_4^+\text{-N kg}^{-1}$ soil) soils of Schleswig-Holstein, namely, Marsch (clayey), Östliches Hügelland (loamy) and Geest (sandy) under a controlled environment. Total $\text{CO}_2\text{-C}$ and $\text{N}_2\text{O-N}$ emissions were significantly higher from Marsch than Östliches Hügelland and Geest. In Marsch, DMPP showed the highest inhibitory effect on $\text{CO}_2\text{-C}$ emission (50%), followed by PIADIN (32%) and ENTEC (16%). In Östliches Hügelland, DCD and PIADIN showed the highest and equal inhibitory effect on $\text{CO}_2\text{-C}$ emission (73%), followed by DMPP (64%) and ENTEC (36%). In Marsch and Östliches Hügelland, DCD showed the stronger inhibitory effect on $\text{N}_2\text{O-N}$ emission (86% and 47%) than DMPP (56% and 30%) and PIADIN (54% and 16%). In Geest, DMPP was more effective in reducing $\text{N}_2\text{O-N}$ emission (88%) than PIADIN (70%) and DCD (33%). Thus, it can be concluded that DCD is a better NI for clay and loamy soils, while DMPP and PIADIN are better for sandy soils to inhibit soil nitrification and gaseous emissions.

Keywords: nitrification inhibitors; soil type; CO_2 and N_2O emissions; soil nitrogen dynamic



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1. Introduction

Nitrogen is an important element for plant growth in agro-ecosystems [1], but the effectiveness of applied fertilizer N in crops rarely exceeds 40% [2]. Chemical N fertilizer constitutes approximately 75% of the total EU input of reactive N [3], and between 40% and 70% of the fertilizer N applied is lost to the atmosphere or the hydrosphere [4]. The majority of applied N is lost from agriculture through ammonia (NH_3) volatilization, gaseous emissions of nitrous oxide (N_2O) and di-nitrogen (N_2) and nitrate (NO_3^-) leaching [5]. Soil NO_3^- -N leaching and N_2O emission are processes responsible for both N losses from agricultural soils as well as environmental pollution [6,7]. Beyond its powerful greenhouse effect, N_2O is also a major ozone-depleting substance involved in the destruction of the protective ozone layer in the stratosphere [8].

The concentration of N_2O , which is about 300 times more reactive a gas than CO_2 , has risen from a pre-industrial value of 270 ppb to 319 ppb in 2005 [9], primarily due to agricultural practices and increased use of industrial fertilizers [1,10]. It has been estimated that agricultural soils produce 2.8 (1.7–4.8) Tg $\text{N}_2\text{O-N}$ year⁻¹ and contribute approximately 65% of the atmospheric N_2O loading [8,9]. In Europe, N_2O emissions from agricultural soils contribute about 70% of the total annual N_2O emissions (European Environment Agency, 2015). Application of N to soils as chemical or organic fertilizers stimulates nitrous oxide (N_2O) emissions, mainly through the processes of denitrification

and nitrification [11,12]. Nitrification is an aerobic process in which ammonium (NH_4^+) is first oxidized to nitrite (NO_2^-) and then nitrate (NO_3^-) [1], and it plays a key role in the soil N cycle [13]. During the oxidation of NH_4^+ to NO_2^- , N_2O can be produced as an intermediate and liberated into the atmosphere [1]. Denitrification is an anaerobic microbial process in which organic carbon is used as an energy source and NO_3^- is reduced to gaseous N compounds, including N_2 and N_2O [14].

Nitrification inhibitors (NIs) are used to improve the efficiency of N fertilizers through decreasing both NO_3^- leaching and gaseous N emissions [14,15]. NIs can decelerate the rate of soil nitrification by deactivating the enzyme ammonia monooxygenase (AMO) responsible for catalyzing ammonia oxidation, the first and rate-limiting step of nitrification, which is produced by ammonia-oxidizing archaea (AOA) and ammonia-oxidizing bacteria (AOB) [16]. As NO_3^- is the initial required substrate for denitrification, the use of NIs decreases N_2O emissions from both processes (nitrification and denitrification) [1].

The production of N_2O , and in turn CO_2 emission, in soil and its inhibition by NIs are complex processes, which can be influenced by different factors such as physicochemical characteristics of the soil. Among these, texture is a major soil characteristic that governs various soil properties, and hence the relative effectiveness of NIs may be different in different textured soils. Soil texture can influence the effectiveness of NIs by affecting their stability/persistence and absorption in soils. Some NIs such as 3, 4-dimethylpyrazole phosphate (DMPP) have been shown to affect N_2O emission by decreasing soil pH [17], which can also vary with soil texture. Some studies have tested the effectiveness of NIs to reduce N_2O emissions but results varied considerably because the studies were carried out under different soil conditions [1]. Thus, it is difficult to draw any specific conclusions about the N_2O mitigation potential of NIs in different textured soils.

This study investigates the effectiveness of four NIs, namely, dicyandiamide (DCD), 3, 4-dimethylpyrazole phosphate (DMPP), nitrogenous mineral fertilizers containing the DMPP ammonium stabilizer (ENTEC) and active ingredients: 3.00–3.25% 1, 2, 4-triazole and 1.50–1.65% 3-methylpyrazole (PIADIN) under three vastly different textured soils (clayey, loamy and sandy). We hypothesized that (i) clay contents would have a positive effect on soil N_2O emissions; and (ii) DMPP would have a better performance than DCD, PIADIN and ENTEC in reducing soil CO_2 and N_2O emissions and the conversion of NH_4^+ -N to NO_3^- -N under a range of soils with different textures. The objective of this study was to evaluate the variation in soil CO_2 and N_2O emissions, and NH_4^+ -N and NO_3^- -N concentrations following the application of the abovementioned NIs in clayey (Marsch), loamy (Östliches Hügelland) and sandy (Geest) soils.

2. Materials and Methods

2.1. Collection, Preparation and Characterization of Soil

Three soils varying in soil texture were collected from the following three geological regions of Schleswig-Holstein, Germany: (1) the sandy outwash region (Geest, the outwash region is dominated by Brunic Arenosols or Cambisols, Podzols and Gleysols, as well as Histosols), (2) the Weichselian glacial region in the east (Östliches Hügelland, the Weichselian glacial deposits contain very fertile Luvisols, Cambisols, Anthrosols derived from colluvic material, Gleysols and Rheic Histosols), and (3) the marshland with alluvial deposits in the west (Marsch, the marshland includes different types of Fluvic Gleysols and Histosols) [18]. The selected soils represent the major soil types or climatic zones of the state of Schleswig-Holstein. The soils belong to three different natural grasslands of the state.

Soils from the upper 20 cm soil horizon were collected. Visible plant residues and stones were removed by passing soil through a 2 mm sieve. A representative subsample of each soil was analyzed for salient characteristics, namely, particle size distribution (clay, sand and silt), pH, total carbon (C) and N, NH_4^+ -N and NO_3^- -N following standard methods (Table 1).

Table 1. Salient characteristics of the experimental soils.

Characteristic	Marsch	Östliches Hügelland	Geest
Silt (%)	10.6 ± 3.9	22.3 ± 9.1	19.2 ± 7.8
Sand (%)	44.3 ± 5.4	62.3 ± 8.7	75.0 ± 6.6
Clay (%)	45.1 ± 3.8	15.4 ± 4.6	5.8 ± 2.3
Texture	clayey	loamy	sandy
Total C (g kg ⁻¹)	20.8 ± 0.34	12.0 ± 0.50	13.2 ± 0.19
Total N (g kg ⁻¹)	1.37 ± 0.01	1.13 ± 0.05	1.11 ± 0.02
NH ₄ ⁺ -N (mg kg ⁻¹)	0.86 ± 0.02	1.39 ± 0.06	3.56 ± 0.06
NO ₃ ⁻ -N	10.9 ± 0.32	13.47 ± 0.59	0.08 ± 0.02
pH	6.00 ± 1.72	7.40 ± 2.45	5.50 ± 2.03

Values (mean ± SE, *n* = 4).

2.2. Incubation Experiment

Four NIs, namely, dicyandiamide (DCD), 3, 4-dimethylpyrazole phosphate (DMPP), nitrogenous mineral fertilizers containing the DMPP ammonium stabilizer (ENTEC) and PIADIN (active ingredients: 3.00–3.25% 1, 2, 4-triazole and 1.50–1.65% 3-methylpyrazole), were tested with the three different soil types (Marsch, Östliches Hügelland and Geest). For comparison, a control without the addition of NI was also included for each soil type. The soils were packed into cylindrical pots (15 cm diameter and 33 cm length, sealed at the bottom) to achieve a bulk density of 1.4 g cm⁻³ with 20 cm depth. The experimental treatments, each having four replications, were arranged in a completely randomized design. All the pots were fertilized with 0.5g NH₄⁺-N kg⁻¹ soil using ammonium sulfate ((NH₄)₂SO₄) salt in solution form. The NIs were applied at 5% of applied NH₄⁺-N (i.e., 25 mg kg⁻¹ soil in solution form). The control treatment involved the application of N fertilizer and deionized water only. Deionized water was added each day to maintain the moisture content equivalent to the water-holding capacity of the soils. Following treatment application, pots were incubated for a period of 57 days in a climatic chamber adjusted to a consistent temperature (15 °C), soil moisture (80% soil water-holding capacity) and air humidity (50%).

2.3. Collection and Measurement of Emitted CO₂ and N₂O

The rate of CO₂ and N₂O emissions was calculated by measuring the concentration of these gases from each pot at different times. The CO₂ and N₂O samples were collected once a day during the first week, once after two days during the second week, and once after three days during the rest of the incubation period. For sampling, the pots were closed first and then gas samples were collected at 0, 20, 40 and 60 min. A 10-mL syringe with a hypodermic needle was used to collect the gas samples. The gas samples were stored in pre-evacuated Chromacol glass vials with chloro-butyl rubber lids that prevent the leakage of gas samples. Each gas sampling was carried out between 09:00 and 11:00 am. Except for the times when gas samples were collected, the pots were left open.

The concentrations of CO₂ and N₂O in the gas samples were measured by gas chromatograph (Agilent 7890A GC, Agilent, CA, USA). The rate of CO₂ and N₂O emissions from each pot (ppm/min) during lid closure was calculated using headspace volume of the pot and a linear relation between CO₂ and N₂O concentrations and time [19]. The flux of CO₂-C (μg h⁻¹ kg⁻¹) and N₂O-N (ng h⁻¹ kg⁻¹) was calculated with the following equation:

$$EN_2O-N = \frac{R \times 60 \times V_{gas} \times AR}{W_{soil} \times V_m} \times 2 \times 1000 \quad (1)$$

$$ECO_2-C = \frac{R \times 60 \times V_{gas} \times AR}{W_{soil} \times V_m} \quad (2)$$

where ECO₂/N₂O is the flux of CO₂-C (μg h⁻¹ kg⁻¹) and N₂O-N (ng h⁻¹ kg⁻¹), *R* is the rate of CO₂ and N₂O emissions from each pot (ppm/min), *V*_{gas} is the gas volume in pot

(L), W_{soil} is the weight of dry soil in pot (kg), AR is the relative atomic mass of C and N, i.e., 12 and 14, respectively, and V_m is the molar volume of gas which is 23.7 L/mol at 15 °C. Total CO_2 and N_2O emissions during the experimental period were calculated from the daily emissions of the gases. The relative lowering of total N_2O emission (%) from NI-treated soils as compared to control was regarded as the efficiency of NIs.

2.4. Analysis of NH_4^+ and NO_3^- in Soil

Soil samples (0–20 cm depth) were collected from the pots on day 1, 15, 29, 43 and 57 of incubation for the measurement of NH_4^+ and NO_3^- concentration. Each soil sample was divided into two subsamples; one was oven-dried at 105 °C for 8 h to calculate water content while the other was used for determination of NH_4^+ and NO_3^- . For the analysis of soil mineral N, 10 g of fresh soil was mixed with 40 mL of 0.0125 M $CaCl_2$ solution (1:4) and shaken for 1 h. After centrifugation for 10 min, the extracts were filtered through Whatman filter paper No. 40 and stored at 4 °C. The extracts were analyzed for NH_4^+ and NO_3^- concentrations using a continuous flow analyzer (San⁺⁺ Automated Wet Chemistry Analyzer—Continuous Flow Analyzer (CFA), Skalar, The Netherlands).

2.5. Statistical Analysis

Soil CO_2 -C and N_2O -N total emissions and NH_4^+ -N and NO_3^- -N concentrations across different incubation times were compared by one-way analysis of variance (ANOVA). Treatment means for total CO_2 and N_2O emissions were compared using two-way ANOVA. The significance of differences between individual means and incubation times was determined using a Tukey's honest significant difference (HSD) test. The statistical analyses were performed by R statistical software (University of Auckland, Oakland, CA, USA) at a confidence level of 95% ($p \leq 0.05$).

3. Results

3.1. Fluxes of CO_2 -C and N_2O -N

Marsch had the highest CO_2 -C flux, followed by Geest and the lowest in Östliches Hügelland (Figure 1). The flux of CO_2 -C progressively decreased with time in all the NI treatments under Marsch and Geest soils (Figure 1). In Marsch, DMPP had the lowest CO_2 -C flux during the incubation period (Figure 1, Table 2). CO_2 -C flux did not differ among the NI treatments during the incubation period in Geest soil (Figure 1). DCD, DMPP and PIADIN had the lowest CO_2 -C flux at 7 days of incubation in Östliches Hügelland soil (Figure 1).

Marsch had the highest N_2O -N flux, followed by Östliches Hügelland and the lowest in Geest soil (Figure 2). Marsch and Östliches Hügelland soils with DCD and ENTEC applied had the lowest and the highest N_2O -N flux, respectively, compared with the other NIs during the incubation period (Figure 2). In Geest, ENTEC showed the highest N_2O -N flux during the incubation period while DMPP and PIADIN showed the lowest N_2O -N flux (Figure 2).

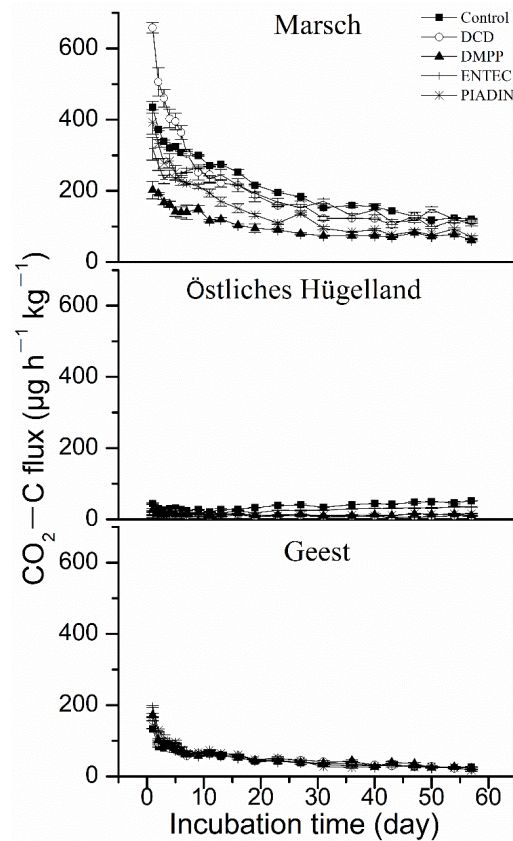


Figure 1. The flux of $\text{CO}_2\text{-C}$ emission as affected by control, dicyandiamide (DCD), 3, 4-dimethylpyrazole phosphate (DMPP), nitrogenous mineral fertilizers containing the DMPP ammonium stabilizer (ENTEC) and active ingredients: 3.00–3.25% 1, 2, 4-triazole and 1.50–1.65% 3-methylpyrazole (PIADIN) treatments in Marsch, Östliches Hügelland and Geest soils. The data points are means of four independent pot replicates, and error bars represent standard errors of the means ($n = 4$).

Table 2. The F test values for $\text{CO}_2\text{-C}$ flux, $\text{N}_2\text{O-N}$ flux, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ under different texture soils with four nitrification inhibitors applied.

Soil Type	Treatment	$\text{CO}_2\text{-C}$ Flux	$\text{N}_2\text{O-N}$ Flux	$\text{NH}_4^+\text{-N}$	$\text{NO}_3^-\text{-N}$
Marsch	Control	0.001	0.016	0.000	0.000
	DCD	0.003	0.014	0.000	0.000
	DMPP	0.045	0.021	0.093	0.089
	ENTEC	0.015	0.040	0.000	0.000
	PIADIN	0.006	0.032	0.000	0.000
Östliches Hügelland	Control	0.013	0.140	0.000	0.000
	DCD	0.085	0.017	0.008	0.007
	DMPP	0.124	0.003	0.000	0.000
	ENTEC	0.004	0.001	0.000	0.000
	PIADIN	0.045	0.017	0.062	0.000
Geest	Control	0.000	0.004	0.001	0.000
	DCD	0.000	0.004	0.000	0.000
	DMPP	0.001	0.011	0.000	0.000
	ENTEC	0.000	0.000	0.000	0.000
	PIADIN	0.001	0.034	0.000	0.002

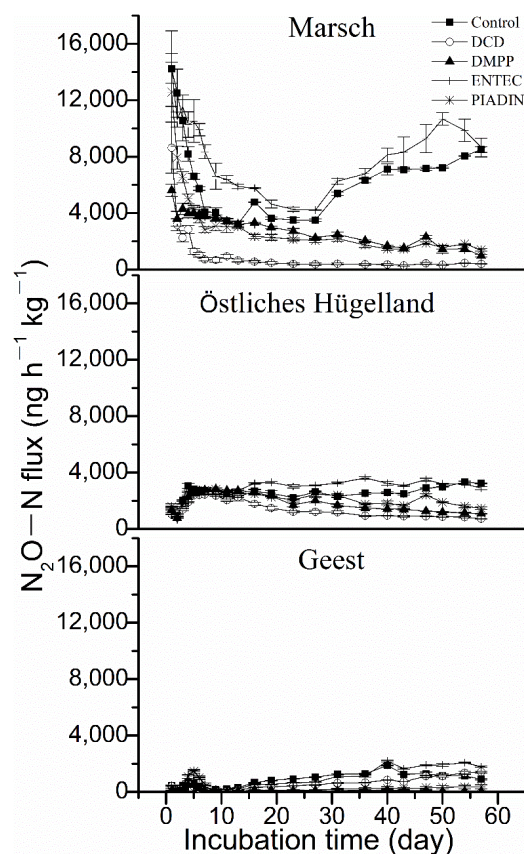


Figure 2. The flux of N_2O-N emission as affected by control, DCD, DMPP, ENTEC and PIADIN treatments in Marsch, Östliches Hügelland and Geest soils. The data points are means of four independent pot replicates, and error bars represent standard errors of the means ($n = 4$).

3.2. Total Emissions of CO_2-C and N_2O-N

Total CO_2-C emission during the incubation period was significantly higher from Marsch soil (274 mg kg^{-1}) than Östliches Hügelland soil (54.6 mg kg^{-1}) and Geest soil (60.3 mg kg^{-1}) (Table 3). In Marsch soil, DMPP showed the highest inhibitory effect on CO_2 emission (50%), followed by PIADIN (32%) and the lowest by ENTEC (16%). DCD did not influence CO_2-C emission from Marsch soil (Table 3). In Östliches Hügelland soil, DCD and PIADIN showed the highest and equal inhibitory effect on CO_2 emission (73%), followed by DMPP (64%) and the lowest by ENTEC (36%). The effect of the NIs on CO_2 emission from Geest soils was nonsignificant.

Table 3. Total CO_2-C emission during the incubation period from Marsch, Östliches Hügelland and Geest soils with control, DCD, DMPP, ENTEC and PIADIN applied under controlled conditions.

NI	Marsch		Östliches Hügelland		Geest	
	Emission (mg kg^{-1})	Decrease (%)	Emission (mg kg^{-1})	Decrease (%)	Emission (mg kg^{-1})	Decrease (%)
Control	$274 \pm 1.3a$	-	$54.6 \pm 2.3e$	-	$60.3 \pm 0.4e$	-
DCD	$261 \pm 11.5a$	5	$14.8 \pm 1.7g$	73	$64.4 \pm 1.2e$	-6.8
DMPP	$136 \pm 3.8d$	50	$19.8 \pm 0.3g$	64	$59.6 \pm 4.4e$	1.2
ENTEC	$231 \pm 11.3b$	16	$35.1 \pm 0.5f$	36	$65.8 \pm 1.4e$	-9.1
PIADIN	$187 \pm 8.4c$	32	$14.5 \pm 1.0g$	74	$65.0 \pm 3.3e$	-7.8

The values (mean \pm SE) are means of four independent pot replicates. The values indicated with the same lowercase letter(s) are not significantly different at $p = 0.05$.

Total N₂O-N emission was also the highest from Marsch soil (8051 µg kg⁻¹), followed by Östliches Hügelland soil (3516 µg kg⁻¹) and the lowest from Geest soil (1313 µg kg⁻¹) (Table 4). In Marsch and Östliches Hügelland soils, DCD showed the stronger inhibitory effect on N₂O-N emission (86% and 47%, respectively) compared with DMPP (56% and 30%, respectively) and PIADIN (54% and 16%, respectively). In Geest soil, DMPP was more effective in reducing N₂O-N emission (88%) than PIADIN (70%) and DCD (33%).

Table 4. Total N₂O-N emissions during the incubation period from Marsch, Östliches Hügelland and Geest soils with control, DCD, DMPP, ENTEC and PIADIN applied under controlled conditions.

NI	Marsch		Östliches Hügelland		Geest	
	Emission (mg kg ⁻¹)	Decrease (%)	Emission (mg kg ⁻¹)	Decrease (%)	Emission (mg kg ⁻¹)	Decrease (%)
Control	8051 ± 279b	-	3516 ± 24d	-	1313 ± 19i	-
DCD	1157 ± 222i	86	1861 ± 102g	47	879 ± 34j	33
DMPP	3533 ± 81d	56	2467 ± 74f	30	157 ± 23k	88
ENTEC	9849 ± 280a	-22	4169 ± 42c	-18	1569 ± 17h	-19
PIADIN	3708 ± 408dc	54	2960 ± 105e	16	387 ± 83k	70

The values (mean ± SE) are means of four independent pot replicates. The values indicated with the same lowercase letter(s) are not significantly different at $p = 0.05$.

3.3. Soil NH₄⁺-N and NO₃⁻-N Concentrations

In Marsch soil, DCD, DMPP and PIADIN slowed down the nitrification process and maintained higher NH₄⁺-N concentration and lower NO₃⁻-N concentration as compared to control (Figure 3; Table 2). ENTEC did not affect NH₄⁺-N and NO₃⁻-N concentrations, which showed the same trend as that of control Marsch soil (Figure 3). NH₄⁺-N concentration decreased and NO₃⁻-N concentration increased progressively during the incubation period in control treatment of Östliches Hügelland soil, whereas DCD, DMPP and PIADIN maintained NH₄⁺-N concentration at high levels and kept NO₃⁻-N at lower levels as compared to control (Figure 3). Similarly, DCD, DMPP, ENTEC and PIADIN slowed down the decrease in NH₄⁺-N and the increase in NO₃⁻-N concentrations as compared to control in Geest soil (Figure 3). DMPP and PIADIN showed lower NO₃⁻-N concentration as compared to DCD and ENTEC in Geest soil (Figure 3).

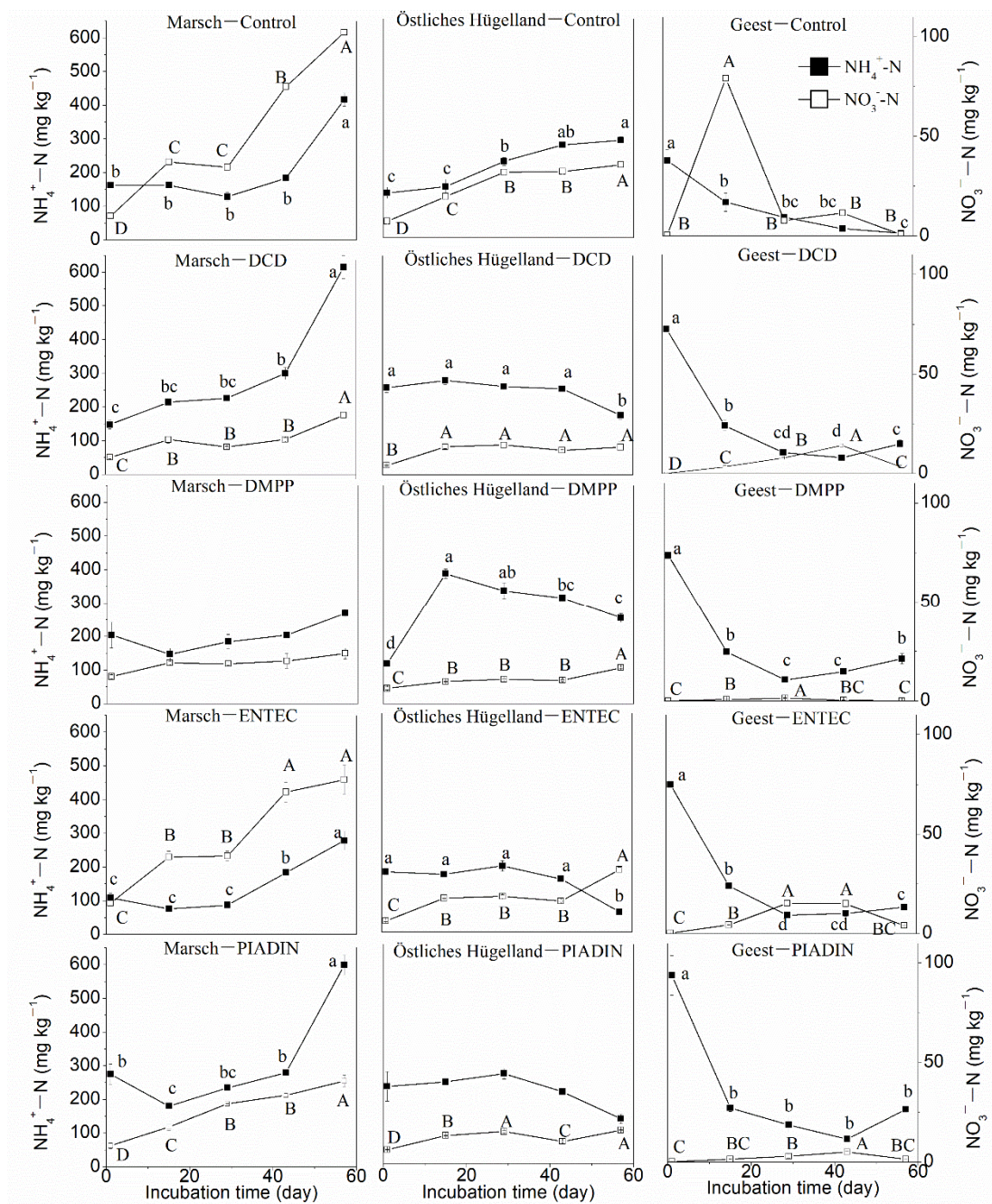


Figure 3. Changes in $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ concentrations in Marsch, Östliches Hügelland and Geest soil with control, DCD, DMPP, ENTEC and PIADIN applied. The data values are means of four independent pot replicates, and error bars represent standard errors of the means ($n = 4$). Incubation times indicated by the same lowercase (NH_4^+) or uppercase (NO_3^-) letter(s) do not differ significantly at $p \leq 0.05$.

4. Discussion

4.1. Effect of Soil Type

Our results showed that $\text{CO}_2\text{-C}$ emission from Marsch soil was higher than from Östliches Hügelland and Geest soils (Figure 1, Table 3). This may be explained by the fact that Marsch soil had more organic matter and clay content than the other soils, and CO_2 emission is positively linked to soil organic carbon (SOC) content [14]. Soil organic carbon content is linearly correlated to soil respiration [20]. Thomsen et al. [21] found that the emission of CO_2 from the sandiest soil was lower than from the heavier textured soils due

to a low content of potentially mineralizable native SOC. Moreover, CO₂-C emissions from native SOC increased with increasing clay content but this relationship was ascribed to the different mineralogy of the soils [22].

Marsch soil showed the highest N₂O-N emission, followed by Östliches Hügelland soil and the lowest by Geest soil (Table 4). Organic C and clay content of the three soils also followed the same decreasing order (Table 1). Microbial community structure of a soil plays an important role in defining the rate of nitrification and denitrification in soil [23], and a soil with higher microbial activity could result in higher N₂O emissions [24]. Nitrogen mineralization and N₂O emissions are influenced by soil organic matter [25] and microbial population [26]. Since nitrification is primarily an autotrophic process, with heterotrophic nitrification accounting for only 20% [27], C-substrate availability and N₂O emissions from denitrification and nitrification are always positively related to each other [28,29]. Abbasi et al. [30] found that the process of denitrification and production of N₂O were smaller in arable soil deficient in organic carbon compared with grassland soil with plenty of organic carbon. Cébron et al. [31] reported that the presence of organic carbon promoted the population of nitrifying bacteria in a clay-textured soil. Thus, higher organic carbon content in Marsch soil could be one possible reason for higher N₂O emission from this soil. Moreover, higher N₂O emission from Marsch than Geest soil may also be explained by the higher pH of this soil. Fan et al. [32] reported significantly higher N₂O emission rates from three alkaline soils (pH 7.6–8.2) as compared to an acidic soil with a pH of 5.6.

Nitrification is also directly influenced by soil texture [25]. A fine-textured soil can retain more water and create more frequent and longer anaerobic conditions than a coarse- or medium-textured soil, and thus may result in faster denitrification and N₂O emission [33]. Overall, the cumulative N₂O-N emission from a clay soil was significantly higher than those from a loamy soil [33] and therefore N₂O emissions increase with increasing clay content.

4.2. Effect of NIs

Except for CO₂-C emission from Geest soil and N₂O-N emission from ENTEC-treated soil, NIs significantly decreased CO₂-C and N₂O-N emissions in all other cases, but the magnitude of the inhibitory effect did not show any specific consistent trend with the soil texture (Tables 3 and 4). Different results have been reported by previous researchers regarding the relative efficacy of NIs in varying textured soils. Barth et al. [18] found that NIs are more efficient in light soils than heavy soils, whereas Akiyama et al. [34] found that the effectiveness of NIs was relatively consistent across the various soil types. According to Fisk et al. [35], the efficacy of DMPP and DCD diminished with the addition of soil organic matter, and Marsden et al. [36] reported decreased efficacy with higher clay content. Volpi et al. [14] found that NIs were effective only in the soil with the highest nitrification activity and the lowest clay content.

In our study, we found that the comparative effectiveness of the NIs in inhibiting CO₂-C and N₂O-N emissions depended on soil type (Tables 3 and 4). DCD had the highest inhibitory effect on soil nitrification in clay soil of Marsch, followed by loam soil of Östliches Hügelland and lowest in sandy soil of Geest (Table 4). Ernfors et al. [37] reported that the efficacy of DCD was soil-specific, whereas Wakelin et al. [38] found that the efficacy of DCD was not related to the soil type. The lowest efficacy of DCD in sandy soil as found in our study may be explained by the lowest decomposition of this NI in sandy soil as compared to heavy textured soils [1]. Moreover, McGeough et al. [7] found that DCD may not be an effective NI under heterotrophic nitrification, which is proportionally the dominant form of nitrification in sandy soil as compared to a heavy textured soil.

DMPP was reported to be highly specific and more effective in inhibiting nitrification as compared to DCD [39]. We found that the inhibitory effect of DMPP on N₂O emission was more pronounced in the sandy soil of Geest than in the loamy and clay soils (Table 4). In short-term incubation experiments, Barth et al. [40] found that decreasing sand content reduced the efficacy of DMPP in retarding NH₄⁺ oxidation. They found that the adsorption

capacity of DMPP is positively correlated with clay content, and that a lower effectiveness of DMPP may be due to the adsorption of the NI on silt and clay particles. In their later study, the same group of researchers reported that DMPP had more pronounced inhibition of N₂O emission in sandy than in loam soil [41]. The same explanation as given above for the effect of DMPP stands true for PIADIN, which showed the same trend of effectiveness in different textured soils as that of DMPP. DMPP has relatively low mobility [39–43], mineralizes slowly and thus has a longer-lasting inhibitory effect on nitrification than DCD [44,45].

Soil texture may affect organic carbon turnover by adsorption of organic carbon onto surfaces of clay or organic complexes [46]. Thus, the effect of different NIs on organic carbon decomposition could also be affected by soil texture. Our results showed that DCD did not influence the soil organic carbon decomposition in Marsch soil, and thus CO₂-C emission from DCD-treated soil was the same as that from control soil (Table 3). DMPP had the best inhibitory effect on the organic carbon decomposition in Marsch soil. The NIs DCD, DMPP and PIADIN effectively inhibited the decomposition of organic carbon in Östliches Hügelland soil and resulted in the lowest CO₂-C emissions (Table 3). ENTEC had the smallest inhibitory effect on the soil organic carbon decomposition in Östliches Hügelland soil.

5. Conclusions

CO₂-C and N₂O-N emissions were higher from N-fertilized clayey soils than from lighter textured loamy and sandy soils. DCD was proven the most effective NI in decreasing CO₂-C and N₂O-N emissions and inhibiting nitrification in the clayey and loamy soils. On the other hand, DMPP and PIADIN could decrease CO₂-C and N₂O-N emissions more effectively in the sandy soil. ENTEC remained the least effective in inhibiting CO₂-C emission, whereas it did not inhibit N₂O-N emission from the studied soils.

It is concluded that clayey soil has more gaseous emissions and NIs perform differently depending on the soil texture to inhibit soil nitrification and gaseous emissions. DCD is a better NI for clay and loamy soils while DMPP and PIADIN are better for sandy soil to inhibit soil nitrification and gaseous emissions. ENTEC is ineffective in all soil textures.

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