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Ammonium-Based Compound Fertilisers Mitigate Nitrous Oxide Emissions in Temperate Grassland

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Abstract: Nitrogen fertiliser application represents the largest anthropogenic source of nitrous oxide (N_2O) emissions, and the magnitude of these emissions is dependent on the type of fertilisers applied in the agroecosystems. Despite N-P-K compound fertilisers being commonly used in agricultural soils, a lack of information exists regarding their effects on N_2O emissions. This study aims at examining the effects of different commonly used N-P-K compound fertiliser formulations with contrasting nitrate to ammonium ratios (0.05 to 0.88) on N_2O emissions, yield, and nitrogen use efficiency (NUE) in temperate grassland and to compare these variables with common straight N fertilisers. Compound fertilisers with varying NPK inclusion rates (18-6-12, 10-10-20, 24-2.2-4.5, and 27-2.5-5), and calcium ammonium nitrate (CAN) and urea + N-(n-butyl) thiophosphoric triamide (NBPT) were applied at 80 kg N ha^{-1} to experimental plots in managed grassland on two occasions in a growing season. Fluxes of N_2O during the experiment period, yield and NUE following two harvests were measured. The cumulative N_2O emission from urea + NBPT, 18-6-12, 10-10-20, and 24-2.2-4.5 treatments were significantly reduced by 44%, 43%, 37%, and 31% compared with CAN treatment under conducive soil moisture condition. Under the same soil condition, 18-6-12 and 10-10-20 treatments showed higher yield, N uptake, and NUE although did not significantly differ from the other fertiliser treatments. Our results suggest that ammonium-based compound fertilisers have a potential to reduce N_2O emissions while maintaining yields. Further long-term study is needed to capture the full magnitude of variations in N_2O emissions, including ammonia (NH_3) volatilization from nitrate and ammonium-based compound fertiliser applications from multiple soil types and under different climatic conditions.

Keywords: nitrous oxide; compound fertiliser; grassland; NBPT; soil moisture

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1. Introduction

Owing to population growth and a change in patterns of food consumption, demand for global food has increased rapidly in recent decades [1]. To satisfy the increasing food demand, the food production system is expected to further intensify, and the use of nitrogen (N) via fertiliser is likely to increase in agricultural soils [2]. Despite N fertilisation leading to increased production, N surplus availability in the soil beyond plant requirement can lead to N losses in the form of nitrate (NO_3^--N) leaching, nitrous oxide (N_2O), nitric oxide (NO), and ammonia (NH_3) emissions, all having a detrimental effect on environment and climate [3]. Nitrous oxide is a major greenhouse gas (GHG) associated with N fertiliser application, with a large radiative forcing and stratospheric ozone-depleting potential [4]. Agriculture soils represent the largest anthropogenic source of N_2O emissions that contribute to approximately 60% of the global total, and this is projected to further increase by 19% by 2030, with the primary source of rise coming from the increasing use of N fertilisers [5]. Grassland constitutes over one-third of the European agricultural land area, making grass one of the most important crops, and most grasslands in Europe are managed intensively for maximum production through fertiliser application [6]. The application of mineral fertilisers has been one of the major causes and drivers of an increase in N_2O emissions in intensively managed grasslands in Europe [7,8].

Nitrous oxide is produced in agriculture soils primarily through microbial processes of nitrification and denitrification, which contribute to 70% of the global emissions in managed and natural soils [9]. Pulses of N_2O emissions from managed grasslands occur after N fertiliser application. However, the extent and timing of the N_2O fluxes depend on fertiliser formulation and rate as well as other soil characteristics and microsite conditions, which are also known to play an important role [10]. Compared to ammonium-based, nitrate-based fertilisers are considered to produce higher N_2O emissions due to the immediate availability of the nitrate substrate for denitrification in wet temperate grassland soils [11–13]. For this reason, changing from nitrate fertiliser to urea plus urease inhibitor-based fertilisers has been put forward in Ireland as an important strategy for reducing N_2O emissions [14]. However, straight urea may lead to N loss via NH_3 volatilization, which can contribute to indirect emissions [13,15]. Relative to calcium ammonium nitrate (CAN), stabilized N fertilisers containing urease and nitrification inhibitors have recently been recommended to increase N use efficiency (NUE) and decrease N_2O release into the atmosphere by reducing the amount of N available for soil microorganisms [12].

Crops compete for available N with microorganisms thus, optimum supply of N to match plants demand ensures high yield and increased NUE, and lowers N_2O emissions. Increasing NUE in fertilisers are associated with a slower release of nutrients by reducing N losses, which is considered to improve yields and mitigate N_2O emissions [16,17]. Although stabilized fertilisers have been formulated to accomplish high yield and NUE by reducing N losses, many findings showed that the effectiveness of these fertilisers are often influenced by environmental conditions, soil characteristics, and management practices [18–22]. Soil moisture is an important factor affecting the magnitude of N_2O emissions from fertilised soil by limiting oxygen concentrations in soil [23] and determining the extent of mineral N accumulations [24]. Several studies reported rapid and peak emissions of N_2O when the water-filled pore space (WFPS) of the soil is greater than 60%, anaerobic soil moisture condition whereby soil NO_3^- is reduced to NO_2^-, N_2O, and N_2 via facultative anaerobic bacteria [10,12,13].

Compound fertilisers contain the complete three macronutrients such as N, phosphorus (P), and potassium (K), and the choice of formulations is guided by the desired nutrient composition. Globally, China is the largest consumer of compound fertilisers where 38% of the applied fertilisers are coming from NPK formulations [25]. In Ireland from 2014 to 2019, compound and straight fertilisers account for 59% and 41% of the total fertilisers used, respectively (Data source: Department of Agriculture, Food and the Marine (DAFM). This figure is substantially higher than the 22% consumption of compound fertilisers in Europe [26], indicating the extensive use of compound fertilisers in Irish soils and contribution to the national GHG budget. Fertilisers with an N-P-K ratio of 10-10-20, 18-6-12, 24-2.2-4.5, 24-2.5-10, and 27-2.5-5 represent the most commonly used fertiliser types, accounting for 77% of the total 80 compound fertilisers has been sold in Ireland in 2019 (DAFM). These fertilisers have different nitrate to ammonia ratios due to their formulation thereby affecting soil inorganic nitrogen pool sizes and consequently influencing the relative availability of ammonium and nitrate for N_2O loss through nitrification and denitrification processes. Additionally, the extra supply of P and K offer a better spatial distribution of nutrients, which might contribute to the N dynamics in soil, is likely to promote crop yield and NUE [27]. Most studies to date have focused on stabilised fertilisers (urease or nitrification inhibitors) as options of decreasing fertiliser related N_2O emissions in agricultural systems, while the potential effects of compound fertilisers with variable nitrate to ammonia ratio composition on N_2O emissions have received little attention. Therefore, it is unclear whether compound fertilisers can offer an alternative source of fertiliser formulation to mitigating or decreasing N_2O emissions in comparison to the most commonly used fertilisers such as urea and CAN.

The primary aim of this study was to quantify N_2O emissions, crop yield, and NUE in a temperate grassland receiving fertilisers formulated with contrasting nitrate to ammonium ratios. There is no a priori body of evidence to assume compound and straight fertiliser applications result in similar yield and N_2O emission factors. Therefore, the secondary objective was to compare compound fertilisers with the common straight fertilisers such as CAN and urea + N-(n-butyl) thiophosphoric triamide (NBPT) with regard to N_2O emissions, yield, and NUE and give an overview of percent (%) N loss for all fertilisers. We investigated compound fertilisers that have varying ratios of nitrate to ammonium from 0.05 to 0.88. We hypothesised that N_2O emissions will be lower for fertilisers with low NO_3^-:NH_4^+ ratios compared to high ratios.

2. Materials and Methods

2.1. Site Description

A field study was conducted at one of the research farms of Teagasc Research Centre at Johnstown Castle, Co. Wexford, Ireland (52°29′22.08″ N, 6°50′07.64″ W) during a growing season of 2020 (June–August). According to Irish soil classification system, the soil at the experimental site is Gleyic Luvisol with parent materials of siliceous stones. The soil type was a sandy loam, with clay, silt, and sand contents of 18.0%, 21.6%, and 60.4%, respectively. The site is a permanent grassland site which was last reseeded in autumn 2018 with perennial ryegrass (*Lolium perenne* L.) with no clover at a seeding rate of 38 kg ha^{-1}. After reseeding, phosphorous (16% P Superphosphate), potassium (50% K Muriate of Potash), and nitrogen fertilisers (27% N CAN) were applied at rates of 10, 40, and 40 kg ha^{-1}, respectively. Weeds were controlled through herbicide application in December 2018, and as a result, negligible weeds presences were detected. For the years before 2018, the plot was permanent grassland (perennial ryegrass) with grazing started in 2013 with dairy replacement stock. The last grazing occurred in September 2019, grazed by spring born calves. Prior to the experiment being established, the site received 150–200 kg N ha^{-1} per year of nitrogen fertiliser, applied in five equal splits between March and September. A description of the soil in the site is presented in Table 1 for soil samples in the top 10 cm taken prior to the commencement of the experiment.

Table 1. Soil characteristics (0–10 cm) of the experimental site with results expressed as mean ± SE (*n* = 8).

Soil Properties	Value
Bulk density (g cm^{-3})	1.30 ± 0.02
pH (1:5 ratio soil to water)	5.40 ± 0.04
Total C (%)	2.26 ± 0.06
Total N (%)	0.24 ± 0.01
C:N	9.33 ± 0.19
Organic C (%)	1.67 ± 0.23
Organic matter (%)	5.70 ± 0.07
[1] available P (mg kg^{-1})	4.64 ± 0.29
[1] available Mg (mg kg^{-1})	82.75 ± 7.91
[1] available K (mg kg^{-1})	140.50 ± 4.54

[1] crop available nutrients were determined using Morgan's extract [28].

2.2. Experimental Design and Treatments

A week before starting the measurements, plots (1.2 m × 1.2 m) were established in a randomized block design, with four blocks and seven fertiliser treatments (Figure 1, Table 2). All fertiliser treatments were replicated four times. Two-meter gaps were left between blocks and plots within blocks for walkways during sampling. The investigated fertilisers consisted of: (i) control (receiving no fertiliser), (ii) N-P-K:18-6-12 (ammonium-based), (iii) 10-10-20 (ammonium-based), (iv) 24-2.2-4.5 (nitrate-based), (v) 27-2.5-5 (nitrate-based), (vii) CAN (nitrate-based), and (vii) urea + NBPT. All fertiliser formulations were applied twice during the experimental period each time at a rate of 80 kg N ha^{-1}, which is a recommended N rate in the region for cut swards. The first fertiliser was applied on 22 June 2020 and the second fertiliser was applied on 21 July 2020. Fertilisers were spread by hand to the chamber bases separately to the rest of the plot area to ensure the accurate N application rate within and outside the chambers. To create conducive conditions [10] for N_2O production during the second fertilisation period, the water filled pore spaces (WFPSs) of the plots were maintained at 70% or above. When the natural rainfall event was not sufficient to attain the required soil water content (>65% WFPS), plots were individually hand-watered using a watering can. The amount of water added to the plots was decided based on the evapotranspiration (ET) data of the last decade of the same period of the experiment, and the three-day rainfall forecast. ET and forecast data were obtained from Met Éireann (Available online: www.met.ie (accessed on 20 July 2020)). The dates and irrigation amounts added are shown in Figure 2. A total of 45 mm water was added at eight applications during the second fertilisation.

Figure 1. Photograph of experimental field (grassland) at Johnstown Castle research site during gas sampling from static chambers with the square collars inserted into the soil and lead covers closed with ballast weights placed on top.

Table 2. Fertiliser formulations and their nutrient contents (%) including nitrate to ammonium ratios.

Fertiliser Formulations	NH_4^+ (%)	NO_3^- (%)	NO_3^-: NH_4^+	N	P	K
18-6-12	11.8	6.2	0.53	18	6	12
10-10-20	9.5	0.5	0.05	10	10	20
24-2.2-4.5	12.8	11.2	0.88	24	2.2	4.5
27-2.5-5	15	12	0.80	27	2.5	5
CAN	13.5	13.5	1	27	0	0
Urea + NBPT				46	0	0

CAN: Calcium ammonium nitrate; NBPT: N-(n-butyl) thiophosphoric triamide.

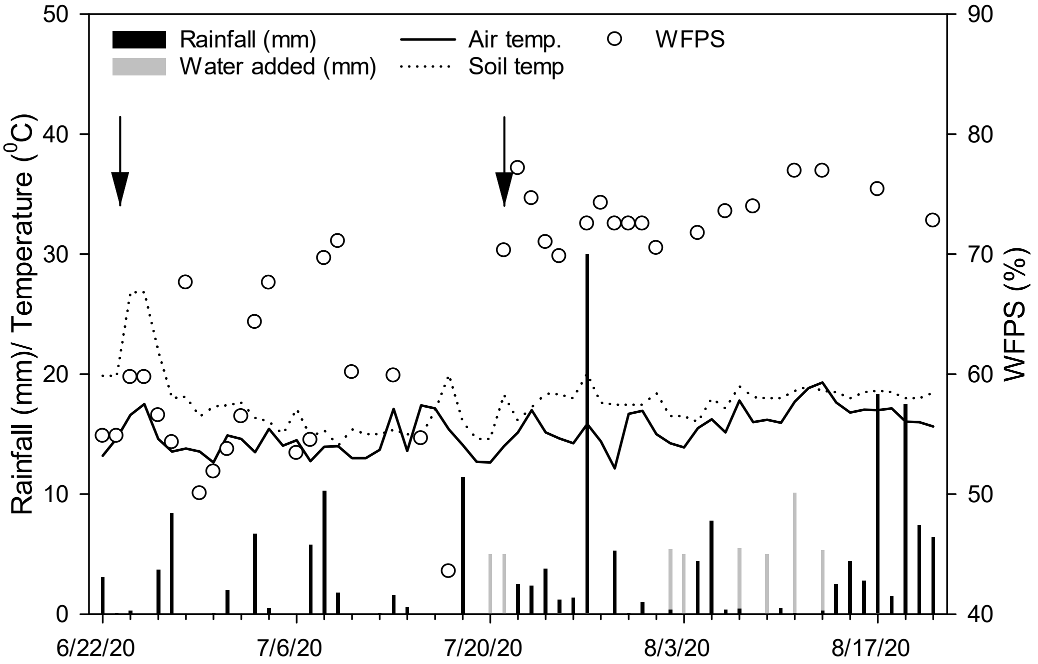

Figure 2. Average air and soil (5 cm depth) temperature, rainfall and water filled pore space (WFPS) over the measurement period. Grey bars represent the amount of additional water applied by hand. Arrows indicate application dates of fertilisers.

2.3. Climatic and Soil Conditions

Rainfall and air temperature were recorded at the meteorological station located 300 m from the study site. Soil volumetric water content was measured on each day of N_2O sampling to a depth of 6 cm using a Theta probe (ML2, Delta-T Devices, Cambridge, UK). Measurements were taken from each plot. Soil bulk density and volumetric water content were used to calculate WFPS.

2.4. Soil Sampling and Analysis

Soil samples were taken to 10 cm depth from each plot using a soil corer on four occasions in each fertilisation event. Top 10 cm is selected because this depth contains a maximum amount of nutrients and major root densities although depths below also play important role in nutrient cycling. Soil cores were placed in a cool-box and taken to the laboratory where samples were analysed on the day of sampling. Mineral N extraction was performed in a 4 mm sieved soil using 2 M potassium chloride (1:5 ratio of soil to solution) after shaking for 1 h. The extracts were analysed colorimetrically for NH_4^+-N and NO_3^--N using an Aquakem 600 discrete analyser (Thermo Electron OY, Vantaa, Finland). Gravimetric moisture content was determined on each day of sampling by drying 20 g of each soil sample for 24 h at 105 °C, which allowed conversion of soil mineral N concentrations into dry weights.

2.5. Nitrous Oxide Sampling and Analysis

From June 2020 to August 2020, N_2O fluxes were measured using the closed static chamber technique using the method described by de Klein and Harvey [29]. A week before starting the measurements, a stainless-steel base collar was installed within each plot to a depth of approximately 5 cm into the soil and 10 cm high upper chamber was prepared for gas sampling (Figure 1). Both collars and chambers have dimensions of 40 cm × 40 cm. Chambers are fitted with two rubber septa. The top rim of the collars contains a channel that is covered with a neoprene stripe. Water was added in the channel followed by a placement of a 10 kg weight in order to ensure airtight sealing in the headspace during sampling. Gas samples were collected at 0 min, 20 min, and 40 min after chamber closure. Linear accumulation of gases in the headspace was assumed; hence the N_2O emissions were calculated based on the rate of change of the gas concentrations during the closure period [30]. Gas samples were taken from the headspaces of the chambers by using 10 mL Luer Lock syringe (Omnifix®, B.Braun Melsungen AG, Melsungen, Germany) fitted with a Terumo hypodermic needle (AGANI™, Hamburg, Germany) and transferred to 7 mL screw-capped vials that were previously flushed with helium and evacuated. Prior to the final sample, the headspace gas was mixed by drawing and releasing air three times. Gas samples were analysed using a gas chromatograph (Bruker CAM, Scion 456-GC, Livingston, Scotland, UK) equipped with a ^{63}Ni electron capture detector (ECD) with high-purity helium as a carrier gas to analyse for N_2O concentrations. Gas sampling took place 5 days a week in the first 2 weeks of fertiliser applications, and frequency of sampling was reduced to 3 days a week in the subsequent weeks. Gas sampling was performed between 10 a.m. and 12 p.m. to get a representative average hourly flux of the day, which was used to calculate daily emissions. Cumulative N_2O emissions were obtained by linear interpolation of the emission values, and integrating the daily gas emissions from each chamber [29]. Cumulative emissions were calculated separately for each fertilisation event because of different soil moisture conditions that constrain variable N_2O production by affecting nitrification and denitrification processes. Percentage of applied N lost as N_2O (N_2O %) gas were calculated by subtracting the cumulative N_2O emissions of the control from the cumulative N_2O emissions of each treatment of the same block, and dividing by the N fertiliser application rate. Yield-scaled (YS) N_2O emissions were computed by dividing the cumulative N_2O emissions over grass growing period by the grass dry matter yield [31].

2.6. Yield, N Uptake and N Use Efficiency

Grass was harvested from each plot to a height of 4 cm, 4 weeks after each fertilisation using grass shears (Art. 8885, Gardena Accu Shears, Gardena, Ulm, Germany). The fresh grass cut from each collar areas weighed and oven dried at 70 °C for dry matter and N content determination. Dry matter content was determined by dividing dry weight by the fresh weight. Grass dry matter yield (expressed in kg ha^{-1}) was computed using fresh weight from the collar area and the dry matter content. Dried samples were ground and subsampled for N content analysis using a C/N elemental analyser (Leco Corp., St. Joseph, Michigan, MI, USA). N uptake was calculated from the dry matter yield and the N content of the dried samples. Nitrogen use efficiency was computed by subtracting the N uptake of control from N uptake of a fertiliser treatment divided by the fertiliser application rate (80 kg N ha^{-1} for each application).

2.7. Statistical Analysis

All statistical analyses were conducted with Minitab Statistical Software (Minitab 19, State College, PA, USA). The effect of different fertiliser treatments on cumulative N_2O emissions was tested for fertiliser applications using general linear mixed model, with fertiliser formulations and application timing as fixed effects and block as a random effect. General linear mixed model was used again to check the effect of fertiliser treatment on dry matter yield, N uptake, NUE and yield-scaled N_2O emissions with fertiliser formulations and harvest as fixed factors and block as a random factor. Variance estimation and F-test for fixed effect were estimated using restricted maximum likelihood and Kenward-Roger approaches, respectively. Normality and homogeneity of variance were verified visually from residual vs. fitted and normal probability plots. Statistically significant differences ($p < 0.05$) were determined from a pairwise comparison of means undertaken using the Tukey HSD test.

3. Results

3.1. Climate and Soil Conditions

The study site naturally received a total of 309 mm of rainfall during June–August, which represents the second wettest growing season of the decade after 2012 when

493 mm was recorded. Average air (soil) daily temperature ranged between 10.1 (11.0) and 19.3 (28) °C with average temperature 14.4 (18.1) and 16.0 (17.8) °C during the first and second fertiliser applications, respectively (Figure 2). The long-term (2010–2019) average air and soil temperature was 14.7 and 17.1 °C, respectively, during June–August. The WFPS ranged between 37.7% and 79.7% (average: 58%) during the first and between 63.2% and 82.4% (average: 73.2%) during the second fertiliser applications (Figure 2).

3.2. Nitrous Oxide Emissions

Daily fluxes of N_2O from the different fertiliser treatments are presented in Figure 3 and cumulative N_2O emissions and yield-scaled N_2O emissions are presented in Figure 4a,c. N_2O flux in control plots ranged from −2.33 to 17.64 g N_2O-N $ha^{-1}d^{-1}$. There was significant interaction effect between fertiliser treatments and application timing. Fertiliser application led to a large rise in N_2O emissions during the two fertilisation periods. Magnitude and frequency of peak emissions were highly coupled to the soil moisture status and the majority fluxes occurred within the first week of fertilisation. In the first fertilisation period, where WFPS is often below 60%, the highest cumulative N_2O emission (0.93 kg N_2O-N ha^{-1}) was observed from 18-6-12 treatment, whereas the lowest fluxes were observed from the urea + NBPT (0.32 kg N_2O-N ha^{-1}) and control (0.04 kg N_2O-N ha^{-1}) (Figure 3). Cumulative N_2O emission from 18-6-12 was significantly higher than 27-2.5-5, urea + NBPT, and control ($p < 0.05$), but not significantly different from the 10-10-20, CAN, and 24-2.2-4.5 (Figure 4a).

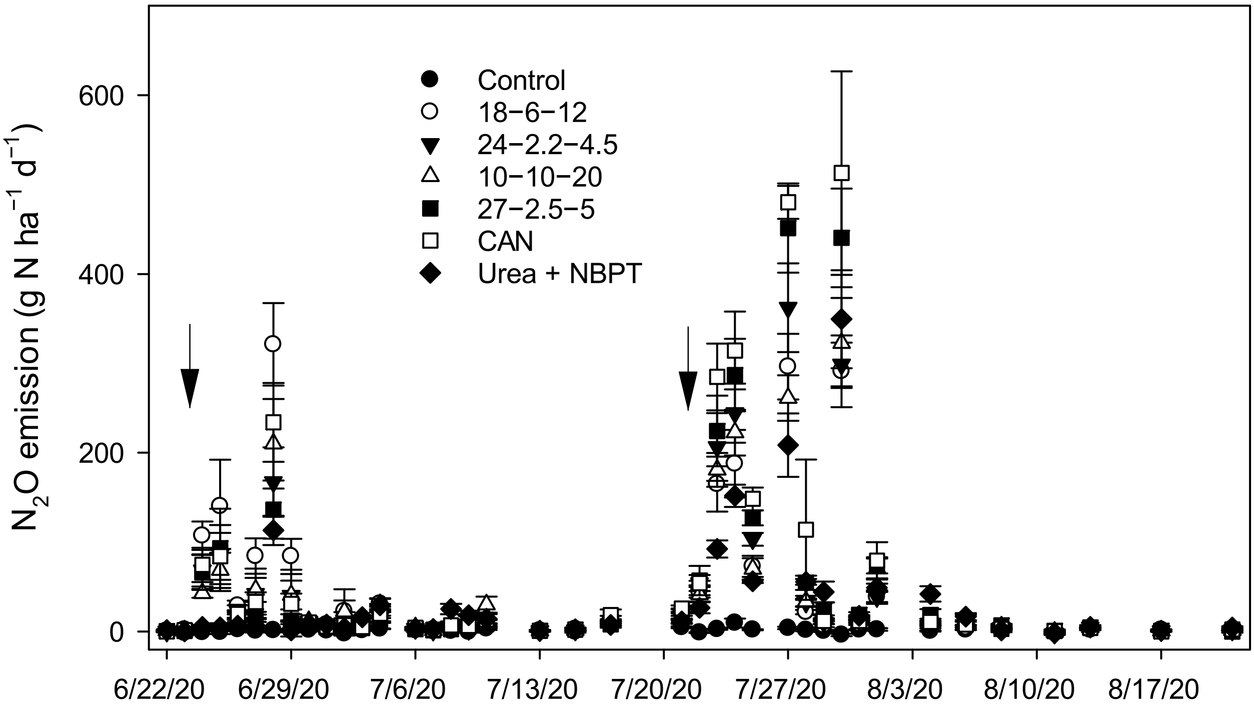

Figure 3. Average temporal N_2O fluxes from different fertiliser formulations applied to a grassland experimental site during a growing season. Arrows indicate applications dates of fertilisers.

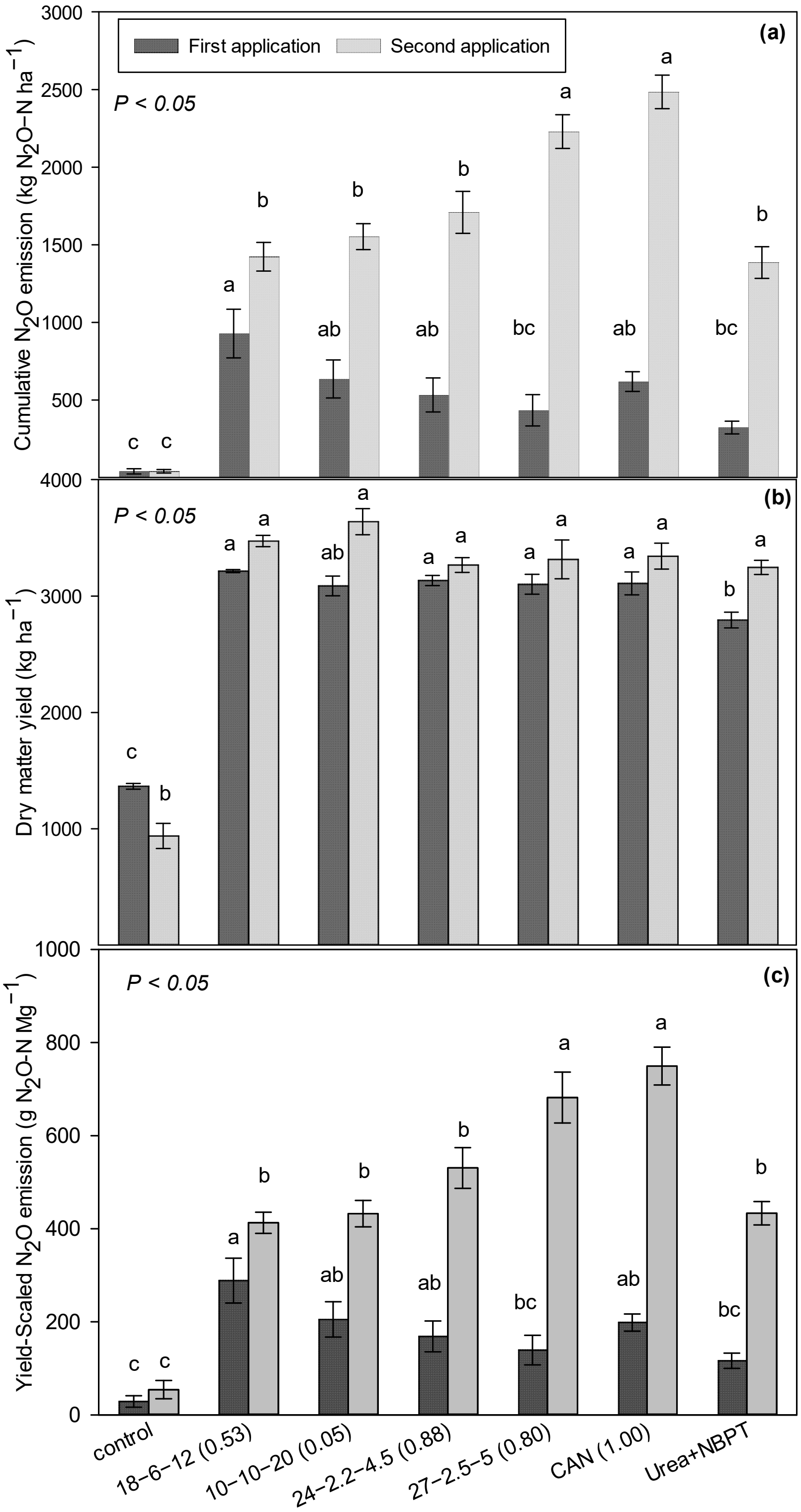

Figure 4. Cumulative N_2O emissions (**a**), dry matter yield (**b**), and yield-scaled N_2O emission (**c**) in the first and second fertiliser application in a growing season of temperate grassland with different fertiliser treatments. Error bars represent standard errors. Statistical differences are based on mixed linear model with the Tukey's HSD post hoc test (95% significance level). Means that do not share a letter are significantly different. Comparisons are between fertiliser treatments within the same N_2O condition. The numbers in parenthesis indicate the NO_3^- to NH_4^+ ratio of the fertilisers.

In the second fertilisation period and much wetter conditions (WFPS generally >70%), CAN and the nitrate-based compound fertilisers 27-2.5-5 and 24-2.2-4.5 produced the highest N_2O emissions compared to urea + NBPT and the ammonium-based compound fertilisers 18-6-12 and 10-10-20 (Figure 4a). Cumulative emissions from CAN and 27-2.5-5 were significantly ($p < 0.05$) higher than the other fertiliser formulations and control. Cumulative N_2O emissions from 24-2.2-4.5, 10-10-20, 18-6-12, and urea + NBPT did not significantly differ from each other; however, the emissions from these treatments were significantly greater than the control ($p < 0.05$) (Figure 4a). In comparison with the first application, all fertilisers in the second application event produced greater cumulative N_2O emissions, with emissions from nitrate and ammonium-based fertilisers resulting in 225 to 417% and 55 to 338% increase, respectively (Figure 4a).

Yield-scaled N_2O emissions showed similar pattern as the cumulative emissions (Figure 4c). With a low yield and N_2O emissions, the control plots showed the lowest yield-scaled N_2O emissions (28.88 ± 12.38 and 54.17 ± 19.68 g N_2O-N Mg^{-1}). Following the first fertilisation, 18-6-12 (288.42 ± 48.17 g N_2O-N Mg^{-1}) and 10-10-20 (204.98 ± 37.76 g N_2O-N Mg^{-1}) whereas in the second, CAN (749.07 ± 40.72 g N_2O-N Mg^{-1}), 27-2.5-5 (681.55 ± 54.49 g N_2O-N Mg^{-1}), and 24-2.2-4.5 (530.38 ± 43.87 g N_2O-N Mg^{-1}) generated higher yield-scaled N_2O emissions. Higher N_2O emissions and equivalent yields in the second fertiliser event compared to the first led to a significant increase of yield-scaled N_2O emissions.

Percentage of N lost as N_2O (N_2O %) were significantly higher following the second fertilisation than the first (Table 3). N_2O % ranged between 0.27% and 1.55% for the first and 1.20% and 3.33% for the second fertiliser applications. Formulation 18-6-12 exhibited the highest N_2O % in the first fertilisation with 1.11 ± 0.18% but was the lowest in the second application with 1.73 ± 0.12% together with the urea + NBPT treatment (1.73 ± 0.20%). The nitrate-based treatments, CAN (3.06 ± 0.14%) and 27-2.5-5 (2.74 ± 0.12%), showed the highest percentage N_2O lost in the wetter condition, differing significantly ($p < 0.05$) from the rest of fertiliser formulations.

Table 3. Mean percentage and standard errors of fertiliser lost as N_2O (N_2O %) for the six fertiliser treatments at two harvests.

Fertilisers	**N_2O % Loss**	
	Harvest 1	**Harvest 2**
18-6-12	1.11 ± 0.18	1.73 ± 0.12
10-10-20	0.74 ± 0.14	1.90 ± 0.11
24-2.2-4.5	0.58 ± 0.15	2.00 ± 0.20
27-2.5-5	0.49 ± 0.12	2.74 ± 0.12
CAN	0.72 ± 0.08	3.06 ± 0.14
Urea + NBPT	0.35 ± 0.03	1.73 ± 0.20

3.3. *Grass Dry Matter Yield and N Uptake*

A significant interaction of treatment and application timing was detected for dry matter yield, but not for N uptake. Fertilisation significantly ($p < 0.01$) increased the grass dry matter yield and N uptake (Figure 4b and Table 4). Thus, the yield and N uptake at the control plots were significantly ($p < 0.01$) lower than all fertiliser treatments (Figure 4b and Table 4). While there were no significant differences in N uptake between any of the fertiliser treatments, dry matter yield in urea + NBPT was significantly lower ($p < 0.05$) than that of 18-6-12, 24-2.2-4.5, 27-2.5-5, and CAN following the first harvest (Figure 4b). Each fertiliser treatment produced a higher yield in the second harvest than the first. In comparison to the first application, the second treatment application resulted in an increase and a decrease in N uptake for ammonium and nitrate-based fertilisers, respectively (Table 4).

3.4. Nitrogen Use Efficiency

Nitrogen use efficiency determined from the second harvest did not differ significantly ($p > 0.05$) from each other, but the NUE for urea + NBPT was significantly lower than 18-6-12 following the first harvest (Table 4). Nitrogen use efficiency for all fertiliser treatments in the second harvest was generally significantly higher ($p < 0.01$) than the first, with the significance ($p < 0.05$) appeared in the two ammonium-based compound fertilisers, 10-10-20 and 18-6-12.

3.5. Soil Mineral N Concentration

The soil NH_4^+-N and NO_3^--N concentrations in the fertiliser treatments are presented in Figure 5a,b for the two fertilisation cycles. Soil NH_4^+-N and NO_3^--N were significantly increased following fertiliser treatments. Fertiliser application increased NH_4^+-N in all fertiliser treatments, with peaks detected for CAN (70.61 ± 10.39 mg kg^{-1}) and urea + NBPT (85.86 ± 16.19 mg kg^{-1}) 9 and 2 days after the first and second applications, respectively. For soils sampled 2 days post-fertilisation, urea + NBPT, CAN, 18-6-12, and 24-2.2-4.5 fertilisers produced higher soil NH_4^+-N in the second application than the first, but 27-2.5-5 and 10-10-20 treatments showed slightly lower NH_4^+-N concentrations. A significant increase in NO_3^--N was observed for all other treatments except for urea + NBPT and 10-10-20, which were only slightly larger than the control. The largest increase in NO_3^--N was detected in the CAN treatment in both fertilisations, with the first application (75.95 ± 10.20 mg kg^{-1}) resulted in twice the amount of the second (37.49 ± 16.70 mg kg^{-1}). Soil mineral N concentrations returned to the pre-fertilisation level within 3 weeks of fertiliser addition.

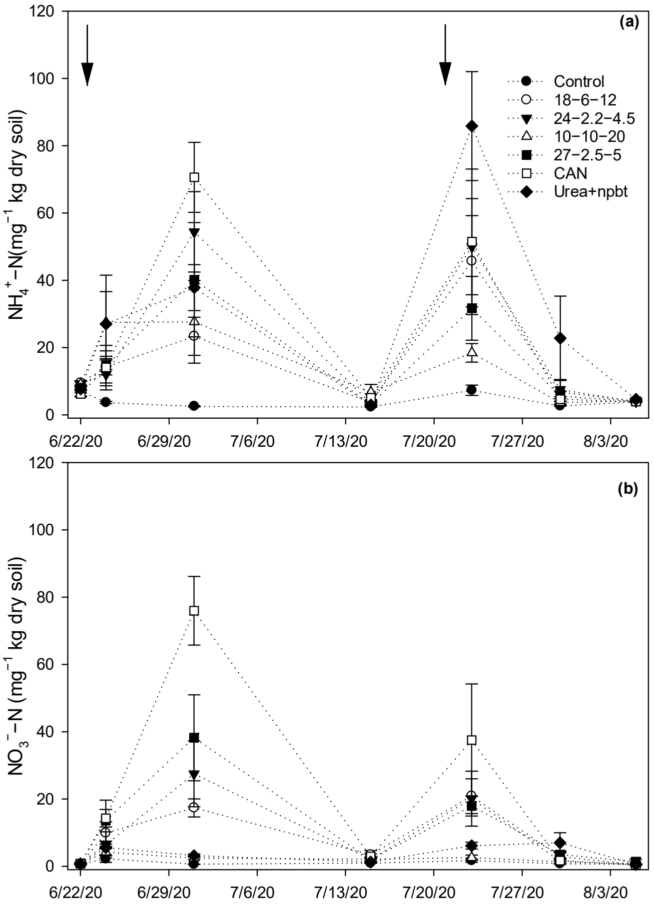

Figure 5. Average soil NH_4^+-N (**a**) and NO_3^--N (**b**) concentrations measured from 0 to 10 cm soil depth during the experimental period. Arrows indicate application dates of fertilisers.

4. Discussion

4.1. The Effect of Fertiliser Formulations on N_2O Emissions

The basis behind stabilised urea formulation in comparison to CAN is to reduce soil NO_3^- concentrations by delaying oxidation of ammonia to nitrate, which may ultimately lead to reductions in N_2O emissions as previously reported in a number of studies [11–13,18,19,32]. The current study examined four compound fertilisers with contrasting nitrate to ammonium ratios as well as CAN and urea + NBPT, and our results showed that significantly lower cumulative N_2O emissions were associated with lower nitrate to ammonia ratios compared to high ratios under high WFPS condition. Ammonium based treatments exhibited higher emissions under low WFPS condition but were not significantly different from the nitrate based fertilisers and had lower magnitude of emissions. Under high WFPS conditions (during the second application), 18-6-12, 10-10-20, 24-2.2-4.5, and 27-2.5-5 treatments produced 43, 37, 31, and 10% lower cumulative N_2O emissions compared to CAN. Compared to CAN, the 18-6-12 and 10-10-20 fertilisers had reductions closest to the 44% N_2O reduction observed in the urea + NBPT. This indicates that ammonium-based compound fertilisers could potentially be a similar mitigation measure to the use of urea + NBPT to reduce N_2O emissions from temperate grassland. The addition of inhibitors incurs extra costs and there are issues around acceptability from farmers and milk processors due to perceptions around residues [20,33]. However, a recent study investigating the potential for residues observed no residue issues associated with the use of NBPT with urea [34].

The major reason for lower N_2O emission from ammonium-based fertilisers in this study can likely be the increased plant N uptake and NUE (see Section 4.2) and reduced risk of denitrification observed during the second fertilisation. Our results are similar to the published reports of Dobbie and Smith [35]; Harty et al. [12] and Krol et al. [13], in terms of ammonium-based (including urea) fertilisers generating lower N_2O emissions in managed temperate grasslands even though these studies used straight fertilisers.

The majority of peak N_2O emission occurred under high soil mineral N and rainfall-induced elevated soil moisture level, which ranged between 65 and 75% WFPS. Increased soil moisture with the available NO_3^- is conducive environmental condition for promoting denitrification and producing high N_2O emission [9]. A strong influence of soil moisture was observed in the two fertilisation cycles, with the second wetter condition resulting in up to 5 and 2.5-fold greater cumulative N_2O emissions in nitrate and ammonium-based fertilisers, respectively. This suggests that the effect of fertiliser formulations in direct N_2O emissions can be vastly variable due to environmental conditions, and notable emission differences between seasons are likely with changing climatic conditions. Harty et al. [12] reported significant reductions of N_2O emissions by switching from CAN to any form of urea in agricultural grassland ecosystems, with substantial differences observed during wet periods. Similar results were reported in Dobbie and Smith [35]; Krol et al. [13]; Smith et al. [36] and Weller et al. [37]. Here, the effect of temperature was minimal for the differences in the emission in the two periods as both fertilisations took place in similar soil temperature conditions (averages: 17.8 and 18.1 °C).

Addition of fertilisers increased soil mineral N concentrations, with the highest NH_4^+ and NO_3^- associated with urea + NBPT and CAN applications, respectively. However, soil NO_3^- levels were lower during the second fertiliser application. This was likely caused by (i) the prevalence of anaerobic soil condition in the second fertilisation, which affects nitrification by delaying the conversion of ammonium to nitrate, (ii) nitrate leaching as a result of heavy rainfall (30 mm) recorded a week after fertilisation, or (iii) increased N acquisition by plants [24]. Importantly the soil NO_3^- concentrations in the urea + NBPT and 10-10-20 treatments were similar to that in the control, with both fertilisers having low N_2O losses compared to CAN.

The percentage of N lost as N_2O across the two applications were significantly affected by the fertiliser formulation, with nitrate-based fertilisers such as CAN and 27-2.5-5 having the highest, while urea + NBPT the lowest, N_2O % loss. Monitoring full-year fluxes is important and recommended to provide emission factors for the less explored compound fertilisers (Table 4).

Table 4. Mean ± SE values of dry matter (DM) yield, N uptake, and Nitrogen use efficiency (NUE) from two individual harvests following fertiliser applications.

Treatment	**Harvest 1**			**Harvest 2**		
	DM Yield (kg ha^{-1}) $p < 0.05$	**N Uptake (kg ha^{-1}) $p < 0.05$**	**NUE (%) $p < 0.05$**	**DM Yield (kg ha^{-1}) $p < 0.05$**	**N Uptake (kg ha^{-1}) $p < 0.05$**	**NUE (%) $p < 0.05$**
Control	1366 ± 24 d	21.1 ± 0.5 c		937 ± 108 d	15.6 ± 1.3 c	
18-6-12	3215 ± 13 abc	81.2 ± 1.1 ab	75.1 ± 1.2 ab	3472 ± 48 ab	85.0 ± 1.6 a	86.8 ± 2.9 a
10-10-20	3087 ± 85 bc	81.9 ± 2.1 ab	76.1 ± 2.6 ab	3640 ± 112 a	85.1 ± 1.1 a	86.8 ± 2.7 a
24-2.2-4.5	3134 ± 43 bc	82.9 ± 2.5 ab	77.3 ± 3.7 ab	3267 ± 64 ab	75.7 ± 3.5 ab	75.1 ± 3.6 ab
27-2.5-5	3101 ± 85 bc	81.8 ± 2.9 ab	73.2 ± 4.7 ab	3316 ± 167 ab	76.5 ± 4.1 ab	77.2 ± 3.6 ab
CAN	3109 ± 98 bc	83.2 ± 1.1 ab	77.7 ± 2.0 ab	3343 ± 111 ab	79.4 ± 1.7 ab	79.7 ± 1.4 a
Urea + NBPT	2794 ± 67 c	72.1 ± 2.0 b	63.5 ± 3.2 b	3246 ± 61 ab	76.7 ± 3.5 ab	75.0 ± 4.3 ab

Means that do not share a letter are significantly different. Statistical significance at $p < 0.05$.

In addition to the differences in the N form, compound fertilisers differ from straight fertilisers by their extra composition of P and K, whose relationship with N and effect on N_2O emissions is not well-established in the literature. O'Neill et al. [38] reported lower N_2O emission from grassland plots receiving P than with no P, with the greater emissions in no P plots hypothetically linked to the dominance of fungi, which lack N_2O-reductase. Long term (25 years) dry matter biomass sampling data from the experimental site of O'Neill et al. [38], which is situated in the vicinity of our study site, shows greater N uptake by plants receiving NPK than NK only (data not shown) suggesting the possibility of P affecting the N dynamics in the soil.

4.2. The Effect of N Formulation on Yield, N Use Efficiency, N Uptake and Yield-Scaled N_2O Emissions

Compared with nitrate-based, ammonium-based compound formulations generally tend to show higher yield and N-uptake. This is particularly evident during the second harvest where N uptake increased in 18-6-12, 10-10-20, and urea + NBPT treatments while decreased in CAN, 24-2.2-5, and 27-2.5-5 (not significantly though). The greater yield in the second harvest may be explained by a slower conversion of NH_4^+ into its oxidised form as a result of denitrifying condition, which enhanced better utilization of nitrogen by the plants. Yield and N uptake of urea + NBPT showed no significant differences with CAN, which is consistent with the results of Harty et al. [21] and Krol et al. [13], despite urea + NBPT showing consistently lower yield and N uptake in comparison with ammonium-based compound fertilisers.

The highest NUE was found in the 10-10-20 and 18-6-12 treatments, which agreed with the DM yield and N uptake results and corresponded with the lowest cumulative N_2O emissions. This would suggest ammonium-based compound fertilisers can be important options for sustaining yield through improved NUE while reducing N_2O emission. NUE values here ranged from 63.5 to 86.8%, with the lowest NUE associated with urea + NBPT. These values are slightly higher than those reported from grassland ecosystems in Krol et al. [13] (49 to 65%), but lower than in Cardenas et al. [39] (>80%). These contrasts may be due to the fact that these studies had longer study periods, varying fertilisation amounts, and used different fertiliser forms.

Yield-scaled N_2O emission was influenced by the fertiliser application, for which 10-10-20 and 18-6-12 treatments showed the highest values in the first application, but low N_2O emissions combined with greater yields caused the lowest YS N_2O emissions in the second application. In the second fertilisation, nitrate-based fertilisers showed the largest YS N_2O with CAN and 27-2.5-5 exhibiting significantly greater YS N_2O with 749.07 ± 40.72 and 681.55 ± 54.49 g N_2O-N Mg^{-1}, respectively. Therefore, ammonium-based fertilisers are more effective with regard to sustaining agronomic benefits by satisfying the nutrient demand of plants, and improving dry matter yield and NUE, while reducing N_2O emissions.

These results are indicative of lower N_2O losses associated with ammonium-based compound fertilisers due to the reduction in the soil nitrate pool. When this coincided with denitrifying conditions, the lower soil NO_3^- results in lower N_2O emissions. This research needs to be up-scaled to evaluate emissions factors for a range of different compound fertiliser over a range of soil types to identify low N_2O emitting fertilisers.

5. Conclusions

The purpose of this study was to evaluate the effect of fertilisers with contrasting NO_3^- to NH_4^+ ratios on N_2O emission in temperate agricultural grassland. N_2O emission in wetter soil was 37–43% and 10–31% lower than CAN for the application of ammonium (10-10-20 and 18-6-12) and nitrate-based (27-2.5-5 and 24-2.2-2.5) compound fertilisers, respectively. Thus, these results suggest that applying ammonium-based compound fertilisers is an additional option for farmers to mitigate N_2O emissions while maintaining production in temperate grasslands. Soil moisture was found to be an important environmental variable controlling the magnitude of the emission, indicating a high prospect of seasonal variability in N_2O emission from these fertiliser forms had this study been held for an extended period. Therefore, further study is needed to capture the full magnitude of variations in N_2O emissions, including NH_3 volatilization from nitrate and ammonium-based compound fertiliser applications from multiple soils and years under different climatic conditions.

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