



Differing effects of increasing calcium ammonium nitrate, urea and urea + NBPT fertiliser rates on nitrous oxide emission factors at six temperate grassland sites in Ireland

Niharika Rahman^{a,*}, Karl G. Richards^a, Mary A. Harty^{a,d}, Catherine J. Watson^{b,c}, Rachael Carolan^c, Dominika Krol^a, Gary J. Lanigan^a, Patrick J. Forrester^a

^a Teagasc, Environment Research Centre, Johnstown Castle, Co. Wexford, Ireland

^b School of Biological Sciences, Queen's University, University Road Belfast, Northern Ireland, BT7 1NN, United Kingdom

^c Agri-Food and Biosciences Institute (AFBI), Newforge Lane, Belfast, Northern Ireland, BT9 5PX, United Kingdom

^d University College Dublin, Ireland

ARTICLE INFO

Keywords:

Climate change
Greenhouse gas emissions
Urease inhibitor
Nitrogen fertiliser
Grassland
N₂O emissions

ABSTRACT

The present study evaluated the impact of three nitrogen (N) fertiliser formulations, applied at five N rates, on nitrous oxide (N₂O) fluxes and annual direct N₂O-N emission factors (EF) in temperate grassland. Closed static chambers were used to measure direct N₂O fluxes at three geographically dispersed locations in Ireland over a two-year period, generating a total of 90 EFs across the six site-years and treatments. The three fertiliser formulations tested were calcium ammonium nitrate (CAN), urea, and urea amended with the urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (NBPT) at 100, 200, 300, 400 and 500 kg N ha⁻¹ yr⁻¹. All treatments were applied in five equal split applications ranging from 20 to 100 kg N ha⁻¹ split⁻¹ over the growing season. The N₂O-N EFs for CAN ranged from 0.39 – 4.68 with a mean of 1.62 (cv. 81 %), for urea from 0.04 – 1.7 with a mean of 0.46 (cv. 77 %) and for urea + NBPT from 0.18 – 1.7 with a mean of 0.60 (cv. 59 %). A significant positive relationship was found between the N rate and the annual N₂O-N EFs in three (CAN), five (urea) and two (urea + NBPT) of six the site-years. For the remainder of the site-years EF was unaffected by N rate. These results indicate that fertiliser N choice and rate can be management factors that enable farmers to alter N₂O losses in temperate grassland. Notably, the response of EF to increasing N rate was not consistent across the fertilisers, with the EF from urea being the most sensitive to the increasing N rate, urea + NBPT the least sensitive and CAN being intermediate. The accuracy of national greenhouse gas accounting could be improved by including N fertiliser formulation and its rate of application. Further research is also needed to understand the inconsistency in EF response to N rate across sites.

1. Introduction

Grasslands play an important role in the global food chain by supplying part of the feed for ruminant animals used for the production of milk and meat (O'Mara et al., 2012). Grasslands are an essential part of the global ecosystem, covering 3.4 billion ha or around 70 % of the world's agricultural area and 22 % of Europe's agricultural land (FAO-STAT, 2017; Hansen et al., 2014). Consequently, practices that are associated with greenhouse gas emissions, including nitrogen (N) fertiliser choice, have a considerable bearing on global emissions and climate. This is particularly the case with the intensification of

grassland-based production systems in order to satisfy the growing requirement for livestock products. Nitrogen is frequently the critical nutrient limiting grass growth, therefore the application of inorganic N fertilisers are regularly needed to optimise pasture production. Nitrogen applications above the agronomic requirement lead to surplus N, which can increase losses through nitrate leaching, ammonia volatilisation, surface runoff and gaseous nitrous oxide (N₂O) emissions to the atmosphere (Garwood and Ryden, 1986; Good and Beatty, 2011; Forrester et al., 2016; Krol et al., 2020; Reay et al., 2012).

Nitrous oxide is a potent greenhouse gas (GHG) that has a global warming potential of around 296 M CO₂ equivalents (Forster et al.,

* Corresponding author.

E-mail addresses: niharika.rahman@teagasc.ie, niharika_agronomy@yahoo.com (N. Rahman).

<https://doi.org/10.1016/j.agee.2021.107382>

Received 20 November 2020; Received in revised form 18 February 2021; Accepted 20 February 2021

Available online 1 March 2021

0167-8809/© 2021 Elsevier B.V. All rights reserved.

2007; IPCC, 2013) and contributes to ozone depletion in the stratosphere (Ravishankara et al., 2009), thus contributing to global climate change. The application of N fertiliser on agricultural soils is one of the key drivers of N₂O emissions and accounts for around 60 % of the world's total agricultural N₂O emission (Reay et al., 2012). Fertilised cut and grazed temperate grasslands contribute more than 10 % of these emissions (EC, 2018; Emmet-Booth et al., 2019). In terms of agriculture in Ireland, N₂O accounts for 35 % of total agricultural greenhouse gas emissions, with grassland occupying 80 % of the agricultural land area (DAFM, 2019). In excess of two-thirds of Ireland's land area is covered by natural or agricultural grasslands, which is the highest proportion in Europe (62 %) (CSO, 2018). The Irish government is committed to reducing the country's GHG emissions by an average of 7 % per year, adding up to 51 % by 2030 to reach carbon neutrality by 2050 (DAFM, 2019). Therefore understanding the implications of N fertiliser choice and rate on N₂O emissions is critical for the accuracy of the GHG inventory and development of mitigation options for grassland agroecosystems in Ireland and globally.

Despite the importance of grasslands and the scale of emissions from this land use, there is relatively little in the literature detailing the influence the form of fertiliser and its rate of application has on N₂O losses from grassland. The loss of N in N₂O emissions in Europe ranges from 0–51 kg N₂O-N ha⁻¹ yr⁻¹ (Hansen et al., 2014; Jones et al., 2005; Kim et al., 2010; Rees et al., 2013). This wide variation seems to be linked to different locations, inorganic N supply and air content of the soil (Clayton et al., 1997; Rees et al., 2013; Smith et al., 2012), greatly determined by local climate, soil type and the management of the farms. While it is generally believed that emissions of N₂O from agricultural soils (arable and grasslands) rise with increasing N fertilisation rates, it has also been noted that the emission factor (EF) is not consistent (increase/decrease/constant) with the rate of N applied (Dai et al., 2013; Hinton et al., 2015; Stehfest and Bouwman, 2006). However, based on the findings from a range of fertilised vs. non-fertilised soils (Bouwman et al., 2002; Stehfest and Bouwman, 2006), the Intergovernmental Panel on Climate Change (IPCC) recommends a default EF value of 1 % for the total N added as inorganic fertilisers, irrespective of the form or rate of application (IPCC, 2006). There is increasing evidence that suggests a non-linear or exponential relationship between N supply and N₂O emission (Cardenas et al., 2010; Hoben et al., 2011; Kim et al., 2010). It has been found that a non-linear increase in direct N₂O emissions leads to N₂O-N EFs which are not constant, but are related to the N supply rates in the soil (Cardenas et al., 2010; Kim et al., 2010). The effect of the N rate on EF is important for how national N₂O loss inventories are estimated, and consequently, this inconsistent effect requires investigation. If the N₂O-N response curve is non-linear, N₂O emissions will be underestimated or overestimated if the IPCC (2006) approach for national GHG inventories are used. Conversely, N₂O mitigation caused by the implementation of lower N fertiliser rates will also be undervalued.

Similarly, fertiliser N formulation has the potential to interact with the rate effect on EF. Harty et al. (2016) report that N₂O-N EF from CAN applied at a single rate (200 kg N ha⁻¹ yr⁻¹) was highly variable across different sites in Ireland, with the highest loss of 3.81 % and an average loss of 1.49 % across the sites. Krol et al. (2020) and Harty et al. (2016) suggest that switching from CAN to urea plus a urease inhibitor could be a good initiative for reducing N₂O emissions from moist temperate grassland. In comparison with CAN, Harty et al. (2016) reported that urea amended with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT), to address the ammonia volatilisation potential of urea, resulted in a lower average N₂O EF of 0.40 % (in a range from 0.21 to 0.69 %) (Krol et al., 2020; Harty et al., 2016). However, there is very little information on how N rate affects the EF for different N formulations, a gap that has been addressed by the present study.

There is a growing call in the scientific community to switch from the IPCC's Tier I system to a more reliable Tier II (country-specific) or Tier III (site-specific) EF system for accurate national greenhouse gas accounting. The aim of the present study was to assess the impact of three

N formulations on daily N₂O fluxes and annual N₂O site-specific EFs at five rates of application in grassland. This work was conducted at three geographically dispersed grassland sites in Ireland over a two-year period (six site-years). The study results will advance the development of N₂O mitigation strategies for grassland and lead to a more accurate national inventory for GHGs.

2. Materials and methods

2.1. Site description

The experiments were established at three locations on the island of Ireland on sites of permanent pasture: Moorepark, Cork (MP); Johnstown Castle, Wexford (JC) and Hillsborough, Down (HB) (Table 1). The experiments were shifted to a separate site at each location in the second year to overcome any carryover effects from the first year and capturing a range of geo-climatic environments, which generated a total of six site-years of data. Thus, three sites x two years herein after referred to as six site-years (e.g. Forrestal et al., 2016; Harty et al., 2016). The sites were selected to cover a variety of locations that are typical of Ireland's grassland soils and climate conditions.

Before the experiment commenced, soil samples (0–10 cm) were collected from each site to determine the general soil characteristics (Table 1). The soil at MP site was sandy loam texture with a total carbon (C) content of 3.01 % and total N content of 0.32 %. The average bulk density of MP sites were 1.1 g cm⁻³ and cation exchange capacity (CEC) was 18 cmol (+) kg⁻¹. The soil at JC site was sandy loam texture with a total C content of 3.0 % and total N content of 0.30 %. The average bulk density of JC sites were 1.2 g cm⁻³ and CEC was 16 cmol (+) kg⁻¹. Whereas, the soil at HB site was clay loam texture with a total C content of 5.6 % and total N content of 0.51 %. The average bulk density of HB sites were 0.83 g cm⁻³ and CEC was 27 cmol (+) kg⁻¹. During the period of gas sampling, on each sampling day soil temperature (5 cm depth), soil moisture and atmospheric pressure were recorded at each site. For each site, daily rainfall and air temperature (Supplementary Fig. 1) data were collected from the nearest (≤ 1 km) meteorological station.

2.2. Experimental setup

A randomised complete block experimental design with five replicates was established at each site. Three fertiliser treatments consisted of increasing rates of calcium ammonium nitrate (CAN), urea, and urea + NBPT from 100 to 500 kg N ha⁻¹ plus a zero N control. The urease inhibitor (NBPT) was coated onto the urea granule (@ 660 ppm NBPT) which was supplied by Agrotain (Koch Fertiliser LLC, USA). Fertilisers were applied at 100, 200, 300, 400 and 500 kg N ha⁻¹, in five equal splits (Table 2) for all the treatments. Prior to each fertiliser application, the grass was cut to 5 cm, weighed and sub-sampled for chemical analysis. To ensure there were no nutrient imbalances, surface application of potassium, phosphorus and sulphur fertilisers were also applied, according to site requirements. Additional information about the experimental setup can be found in Harty et al. (2016). The agronomic performance at each of the sites is reported by Forrestal et al. (2017).

2.3. Measurement of N₂O fluxes

The closed static chamber technique was used to measure N₂O fluxes over a 12-month period (Chadwick et al., 2014). The chambers were made of stainless steel comprised of two parts: a chamber base of 40 cm × 40 cm wide and 10 cm high and a lid of 40 cm × 40 cm × 10 cm high. The bases were inserted (depth of ≥ 5 cm) into the soil three days before the gas sampling commenced. The chambers were designed consistently across all the sites. As recommended by Reeves and Wang (2015), gas sampling was commenced in the hours between 10 am – 2 pm. For each N₂O sampling event, five chambers at the MP and JC sites and three

Table 1
Location, measurement periods, climate and soil physical and chemical properties for six site years.

Sites	MP 2013	MP 2014	JC 2013	JC 2014	HB 2013	HB 2014
GPS coordinates	52°9'27"N, 8°14'42"W	52°9'33" N, 8°14'43"W	52°18'27"N, 6°30'14"W	52°17'32"N, 6°30'7"W	54°27'82"N, 6°04'57"W	54°45'12"N, 6°04'57"W
Measurement period	March 2013- March 2014	March 2014- March 2015	March 2013- March 2014	March 2014- March 2015	March 2013- March 2014	March 2014- March 2015
Soil textural class ^a	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Clay loam	Clay loam
Sand (%)	59	58	53	52	41	43
Silt (%)	28	28	33	34	34	35
Clay (%)	14	14	14	14	25	22
Bulk Density ^b	1.02	1.18	1.11	1.27	0.86	0.79
Soil pH	5.55	5.37	5.53	5.69	5.74	5.60
Total Nitrogen (%)	0.32	0.32	0.31	0.28	0.56	0.45
Initial soil NO ₃ ⁻ (mg/kg)	6.70	5.95	2.90	1.30	2.75	3.78
Initial soil NH ₄ ⁺ (mg/kg)	4.00	6.01	1.90	3.90	5.91	2.17
Soil Total Carbon (%)	3.00	3.02	3.16	2.83	5.99	5.16
Soil organic carbon (%)	2.98	3.00	2.78	2.78	5.94	5.12
Soil loss on ignition (%)	7.40	7.90	7.30	7.02	14.3	12.5
CEC (cmol(+) kg ⁻¹)	16.7	18.4	15.6	15.5	28.5	25.4
Annual Rainfall (mm)	1130	1002	1021	939	1113	1047
Growing season rainfall(mm)	407	459	336	441	560	478
30 year average growing season rainfall (mm)	478	509	512	534	478	478

^a Soil texture classification determined using LandIS portal© Cranfield University, UK.

^b Soil sampled to 7.5 cm at HB and to 10 cm at JC and MP, Stone free Bulk density sampled to 20 cm at all sites.

Table 2
Fertiliser N application rates (kg N ha⁻¹) and date of split application for each treatment.

Annual rate	N application rates kg N ha ⁻¹					N application dates					
						MP site		JC site		HB site	
	100	200	300	400	500	2013	2014	2013	2014	2013	2014
Split 1	20	40	60	80	100	19/03	10/03	19/03	10/03	11/03	24/03
Split 2	20	40	60	80	100	29/04	28/04	29/04	28/04	15/04	06/05
Split 3	20	40	60	80	100	27/05	03/06	27/04	03/06	20/05	09/06
Split 4	20	40	60	80	100	01/07	07/07	01/07	07/07	24/06	28/07
Split 5	20	40	60	80	100	26/08	18/08	26/08	18/08	19/08	08/08

chambers at the HB sites were randomly chosen on each sampling day to check the linearity ($\geq 90\%$ of the observations were linear) of the accumulation of N₂O emission within the chamber headspace. For these chambers, gas samples were taken at 0, 15, 30, 40 and 60 min intervals, in line with the methodology of Chadwick et al. (2014). For each sampling plot, headspace gas samples were taken at 40 min after closing the chamber. For all headspace N₂O calculations, ambient air samples were used as the time zero (T₀) N₂O estimate, in line with Chadwick et al. (2014) who demonstrated that the use of ambient air samples as a substitute for gas chamber T₀ headspace samples, did not cause any bias for the calculation of N₂O emissions (Harty et al., 2016). This sampling approach, which is explained in detail and justified by Chadwick et al. (2014), was chosen to maximise chamber numbers to capture spatial N₂O loss variability in this large study that collected measurements from 480 experimental units across the six site-years. The gas samples were collected using a syringe (10 mL at MP and JC, 20 mL at HB) and injected into pre-evacuated 7-ml gas vials at MP and JC, and 12 mL gas vial at HB. Gas samplings were undertaken for four times a week in the first two weeks after fertiliser application. Sampling frequency was reduced to two days per week for the subsequent two weeks and then one day per week up until the following fertiliser application campaign. During the winter period, once N₂O fluxes had returned to their baseline levels, gas sampling was reduced to a fortnightly frequency.

2.4. N₂O analysis and calculation

The N₂O concentrations in the gas samples from MP and JC sites were determined by using a Bruker 456 gas chromatograph (GC) equipped with a ⁶³Ni- electron capture detector. At the same time, samples from HB sites were analysed by a Bruker 450 GC- electron

capture detector. An automatic Swiss Combi-Pal sampler (CTC Analytics AG) was used to inject the gas samples into the GC (Harty et al., 2016). N₂O-N emissions were computed according to the adapted equation (Kelliher et al., 2013) as follows:

$$F = (\Delta C/\Delta t) \times (V/A) \times ((P \times M)/(T \times R))$$

Here, F is the N₂O-N flux rate (g m⁻² day⁻¹), ΔC (ppbv) is the concentration change in the gas chamber headspace for the duration of the enclosure period, whereas Δt is time interval (40 min), $\Delta C/\Delta t$ is the slope for T₀ and T₄₀, V (m³) is chamber volume, A (m²) is the chamber area (soil surface area), P is the pressure of the atmosphere (Pa), M is the molar mass of the gas (28 g N₂O-N mol⁻¹), T is the average temperature (°K) and R is the constant for ideal gas (8.314 J K⁻¹ mol⁻¹). The cumulative emissions of N₂O (N₂O-N) were computed separately (for each replicate per treatment) by integrating the area under the curve of each measurement point. The trapezoid formula was used to calculate the area between the two adjacent intervals on the measurement days as follows (de Klein and Harvey, 2012; Rahman et al., 2019):

$$At(ab) = (t_b - t_a) \times (F_{ta} + F_{tb})/2$$

Here, At (ab) is the calculated area of the two adjacent intervals (between t_a and t_b) on the measurement days (g m⁻²), t_a and t_b are the number of days from the start of the experiment of the two adjacent measurements. F_{ta} and F_{tb} are the N₂O-N fluxes (g m⁻² d⁻¹) on t_a and t_b.

For all time intervals, the total cumulative emissions of N₂O (N₂O-N) were calculated as the sum of emissions at (ab).

The N₂O-EF were computed from different treatments by using the equation suggested by the IPCC (2006) as follows:

$$EF_N = \left(\frac{\sum N_{N_2O} - \sum N_{Control}}{N_{appl}} \right) \times 100$$

where EF_N is N_2O -N emission factor, $\sum N_{N_2O}$ is the total cumulative N_2O -N emissions from each treatment, $\sum N_{Control}$ is the total cumulative N_2O -N emissions from control and N_{appl} is the total N fertiliser applied, all N expressed in $kg\ ha^{-1}$.

2.5. Statistical analysis

Statistical Analysis System (SAS) software 9.4 for Windows (SAS Institute, 2002–2012) was used for statistical analyses. Normality of variances were checked by using the Shapiro–Wilk test and homogeneity were checked by using the Levene's test. Analysis of variance (ANOVA) were used to determine the differences between the treatments' (effect on total cumulative N_2O emission) by using the general linear models (GLM) procedure in SAS. Significance was determined at an alpha level of 0.05. In the cases where ANOVA was significant, means were compared by using the F-protected least significant difference test. To determine the correlations coefficient between selected variables, PROC CORR procedure was used for Pearson correlation coefficients analysis. Simple linear regression was also done to estimate the association between the different rates of N fertilisers and the N_2O -N EFs.

3. Results

3.1. Temporal dynamics of nitrous oxide fluxes

The temporal dynamics of N_2O fluxes are presented in Fig. 1. Nitrous oxide dynamics over the two-year sampling were considerably affected by the type and rate of fertilisers and by the sites themselves (Fig. 1). The most pronounced peaks in N_2O emissions were associated with fertiliser applications. The magnitude of the peaks differed between fertiliser formulations, rates of N applied and experimental site (Fig. 1).

At the MP site-years the highest average daily N_2O fluxes from CAN, urea, urea + NBPT and control were 168 g, 190 g, 228 g and 11 g N_2O -N $ha^{-1}\ d^{-1}$, respectively. The urea + NBPT treatment at 400 $kg\ N\ ha^{-1}\ yr^{-1}$ showed the highest average flux (228 g N_2O -N $ha^{-1}\ d^{-1}$) after the third split of fertiliser N in June, 2014 (Fig. 1). At the JC site-years the highest average daily N_2O fluxes were 409 g, 163 g 147 g and 58 g N_2O -N $ha^{-1}\ d^{-1}$ from the CAN, urea, urea + NBPT and control treatments (Fig. 1), respectively. The highest average daily N_2O flux (409 g N_2O -N $ha^{-1}\ d^{-1}$) from all treatments at JC sites was from the 400 $kg\ N\ ha^{-1}\ yr^{-1}$ CAN applied after the first split of application (80 $kg\ N\ ha^{-1}$) in March, 2013 (Fig. 1). At the HB sites, the highest average daily N_2O fluxes were 1890 g from CAN, 330 g from urea, 1456 g from urea + NBPT and 12 g N_2O -N $ha^{-1}\ d^{-1}$ from the control (Fig. 1). The highest average daily N_2O fluxes throughout the experiment were at the HB site during 2013, which was 1890 g N_2O -N $ha^{-1}\ d^{-1}$ (Fig. 1). This large peak occurred after the fourth day of the fourth split of fertiliser N (80 $kg\ N\ ha^{-1}$) on 28 June from the 400 $kg\ N\ ha^{-1}\ yr^{-1}$ CAN treatment. On the same occasion, losses from the 80 $kg\ N\ ha^{-1}$ application were 200 and 233 g N_2O -N $ha^{-1}\ d^{-1}$ for urea and urea + NBPT, respectively (Fig. 1).

3.2. Cumulative emissions of nitrous oxide

Table 3 shows the cumulative emissions for all treatments and sites. Total cumulative emission at each experimental site was significantly ($P < 0.05$) affected by both the N rate and the formulations (Table 3, Supplementary Fig. 2). Total cumulative emissions were significantly higher at the HB sites than at the JC and MP sites in both 2013 and 2014.

Across all sites, CAN had significantly higher N_2O losses than urea and urea + NBPT, except when applied at 100 $kg\ N\ ha^{-1}\ yr^{-1}$ (Table 3). At MP sites, emissions from CAN were only significantly higher than urea-based formulations when applied at 300 $kg\ N\ ha^{-1}$ in 2013 and at 200 $kg\ N\ ha^{-1}$ in 2014. The highest total cumulative emission at MP was

4.28 $kg\ N_2O$ -N ha^{-1} from CAN at 300 $kg\ N\ ha^{-1}$ in 2013.

At the JC site in 2013, CAN showed significantly higher cumulative N_2O emission than Urea and urea + NBPT treatments only when applied at 300 and 400 $kg\ N\ ha^{-1}$ (Table 3). In 2014, CAN showed significantly higher N_2O emissions than the urea-based formulations at the higher rates (300, 400 and 500 $kg\ N\ ha^{-1}\ yr^{-1}$).

CAN and the high N rate treatments (Table 3) dominated the total cumulative N_2O emissions at the HB sites (Table 3). CAN application showed significantly higher cumulative emissions than those from urea and urea + NBPT, apart from at the rate of 100 $kg\ N\ ha^{-1}$ applied in the year 2014. The lowest cumulative emission from all sites (ranging from 0.37 – 0.98 $kg\ N_2O$ -N ha^{-1}) was always observed from the control treatments in both years (Table 3).

3.3. Emission factors of nitrous oxide

Nitrous oxide EFs, expressed as a % of total N applied are shown in Table 3. In total, 90 separate N_2O EFs were generated across three fertiliser products, five N rates and six site-years. For CAN, EFs ranged from 0.39 – 4.68 (Table 3) with 18 out of 30 observed EFs above the IPCC default value for N fertiliser of 1 % and 12 below this value. The mean EF for CAN across rates and site-years was 1.62 % and the median EF was 1.13 %. For urea, EFs ranged from 0.04 to 1.70 with just one of 30 observed EFs above the IPCC default value of 1 % and 29 below this value. The mean EF for urea across rates was 0.46 % and the median 0.38 %. For urea + NBPT, EFs ranged from 0.18 to 1.70 with again just four of 30 EFs above the IPCC default value of 1 % and 26 below this default value. The mean EF for urea + NBPT across rates and site-years was 0.6 % and the median 0.62 %.

The relationship between the N rate and the EF for each N fertiliser at each of the six site-years is shown in Table 4 and Fig. 2. The test of the relationship between N rate and EF revealed a difference between fertilisers. For CAN in three of six site-years the EF was not affected by N rate as indicated by the absence of a significant slope in the relationship (Table 4). At the other three site-years, a significant positive relationship was found between N rate and EF (Table 4). In contrast, for urea, although EFs were lower than for CAN, the urea EFs showed a significant positive relationship with increasing N rate in five out of six site-years (Table 3). The EF for the urea + NBPT was the least impacted by N rate with a positive slope in the relationship between N rate and EF detected in only two of six site-years (Table 4).

4. Discussion

4.1. The influence of different N formulations on N_2O emissions

Over the two years of the study, there were higher overall cumulative N_2O emissions and N_2O -N EFs from CAN compared with the urea based formulations, in 26 out of 30 comparisons (Table 3). For CAN, EFs ranged from 0.39 to 4.68 % compared to 0.04–1.70 % for urea and 0.18–1.70 % for urea + NBPT (Table 3). A large range in EFs for CAN (0.57–3.81 %) has also been reported in previous studies in Irish grasslands conducted at a single N rate (Krol et al., 2020; Harty et al., 2016; Hyde et al., 2006). In contrast, in a literature review based on studies in Brazil, Mazzetto et al. (2020) reported that non-urea fertilisers (ammonium nitrate (AN) and ammonium sulphate) have, on average, a 61 % lower N_2O -EF than urea fertilisers. IPCC suggests a default EF of 1 % for N additions from inorganic fertilisers regardless of their form and rate of application (IPCC, 2006). However, the present study shows that there are clear differences between fertiliser N formulations and rates and that the IPCC value of 1 % is only a very coarse first estimate of what actually occurs on the ground. The present study on Irish temperate grassland is unique in providing greater insight into fertiliser formulation and rate effects on EFs. This type of work is urgently needed to develop and implement strategies to address the climate challenge. In the case of urea, only one out of 30 EFs was above the IPCC default

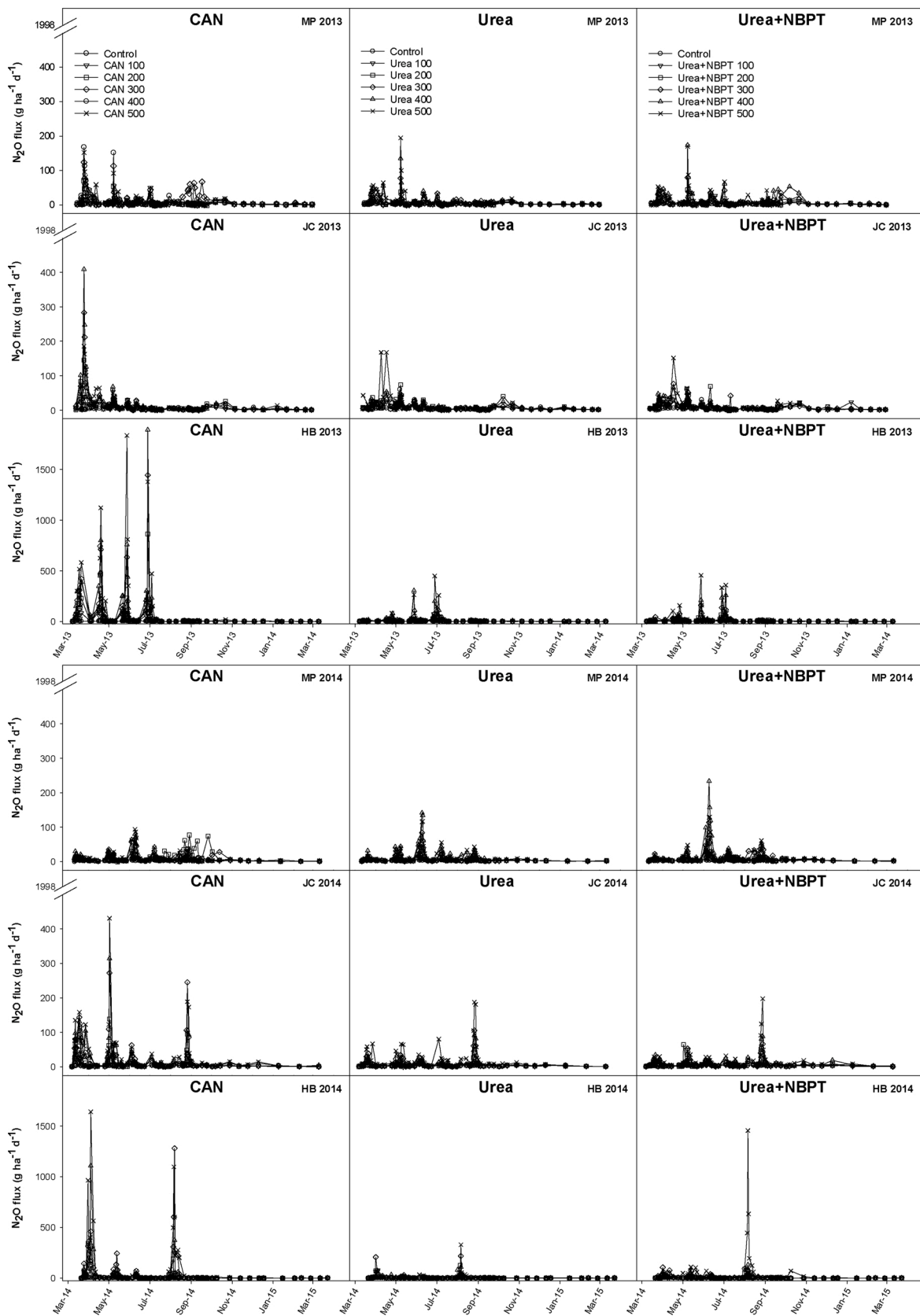


Fig. 1. Average daily N₂O flux (g ha⁻¹) from five N application rates with three N formulations at six site-years in Ireland. Arrows indicate the application of fertiliser. Error bars are omitted for improved clarity. Note: Differences in N₂O flux scale for improve clarity.

Table 3
Cumulative N₂O-N emission (kg ha⁻¹) and emission factors (%) from five N application rates at six site-years in Ireland.

Fertilisers	Cumulative emission (kg ha ⁻¹)							Emission factor (%)						
	MP		JC		HB		Mean	MP		JC		HB		Mean
	2013	2014	2013	2014	2013	2014	(all sites)	2013	2014	2013	2014	2013	2014	(all sites)
Control (0)	0.89e	0.73e	0.98g	0.93f	0.48h	0.37e	0.73e	–	–	–	–	–	–	–
CAN 100	1.43de	1.12cd	1.64efg	1.37def	3.66e	1.70e	1.82de	0.54	0.39	0.66	0.44	3.18	1.33	1.09
Urea 100	0.96e	0.91de	1.02efg	0.99f	0.74g	0.87e	0.91e	0.06	0.18	0.04	0.06	0.26	0.50	0.18
Urea + NBPT 100	1.15e	1.02cde	1.16efg	1.12def	0.73g	0.63e	0.97e	0.26	0.29	0.18	0.19	0.25	0.26	0.24
CAN 200	2.05cde	3.60ab	2.59def	2.23cd	8.09d	3.72cd	3.71c	0.58	1.44	0.81	0.65	3.81	1.68	1.49
Urea 200	1.09e	1.30cde	1.45fg	1.12def	1.08g	1.35e	1.23de	0.10	0.28	0.24	0.10	0.30	0.49	0.25
Urea + NBPT 200	1.32e	1.54cd	2.36def	1.68ef	1.21g	1.13e	1.54de	0.22	0.41	0.69	0.38	0.37	0.38	0.41
CAN 300	4.28a	4.03a	4.09bc	4.58bc	13.87c	7.42bc	6.38b	1.13	1.10	1.04	1.22	4.46	2.35	1.88
Urea 300	1.98cde	1.93bcd	1.93efg	1.93de	1.26g	2.44de	1.91de	0.36	0.40	0.32	0.33	0.26	0.69	0.39
Urea + NBPT 300	2.39bcde	3.82ab	2.84de	1.93de	2.88fg	2.50cd	2.73cd	0.50	1.03	0.62	0.33	0.80	0.71	0.66
CAN 400	3.77ab	3.50ab	5.39a	5.42b	17.57b	10.19b	7.64b	0.72	0.69	1.10	1.12	4.27	2.46	1.73
Urea 400	2.40bcde	4.67a	2.67de	2.03cd	3.52f	4.05cd	3.22c	0.38	0.98	0.42	0.28	0.76	0.92	0.62
Urea + NBPT 400	3.92ab	5.75a	3.46cd	1.76de	3.55f	4.10cd	3.76c	0.76	1.25	0.62	0.21	0.77	0.93	0.75
CAN 500	3.52abc	4.63a	4.85ab	7.44a	23.90a	16.96a	10.22a	0.53	0.78	0.77	1.30	4.68	3.32	1.90
Urea 500	3.06abcd	5.00a	4.80ab	4.81bc	4.09e	8.88bc	5.11bc	0.43	0.85	0.76	0.78	0.72	1.70	0.88
Urea + NBPT 500	3.77ab	5.08a	4.41ab	4.81bc	5.48e	8.87bc	5.40bc	0.58	0.87	0.69	0.78	1.00	1.70	0.93

CAN= Calcium Ammonium Nitrate; NBPT= N-(n-butyl) thiophosphoric triamide. MP= Moorepark; JC= Johnstown Castle; HB= Hillsborough sites. Values with different letters (a to g) within a column indicate significant differences ($P < 0.05$) between treatments (CAN, Urea and Urea+NBPT) and fertiliser rates.

Table 4
Relationship between N treatments and nitrous oxide emission factors.

Treatments	R ²	Equations	P value
MP 2013			
CAN	0.01	y=0.0001x+0.67	0.90
Urea	0.88	y = 0.0010x-0.04	0.02
Urea + NBPT	0.68	y = 0.0012x+0.11	0.08
MP 2014			
CAN	0.01	y = 0.0003x+0.87	0.98
Urea	0.82	y = 0.0020x-0.07	0.03
Urea + NBPT	0.60	y = 0.0020x+0.17	0.12
JC 2013			
CAN	0.19	y = 0.0005x+0.72	0.47
Urea	0.93	y = 0.0016x-0.13	0.01
Urea + NBPT	0.49	y = 0.0010x+0.28	0.19
JC 2014			
CAN	0.84	y = 0.0022x+0.28	0.03
Urea	0.80	y = 0.0016x-0.18	0.04
Urea + NBPT	0.45	y = 0.0010x+0.08	0.22
HB 2013			
CAN	0.84	y = 0.0035x+3.03	0.03
Urea	0.72	y = 0.0014x+0.05	0.07
Urea + NBPT	0.90	y = 0.0019x+0.07	0.01
HB 2014			
CAN	0.96	y = 0.0048x+0.80	0.01
Urea	0.80	y = 0.0028x+0.01	0.04
Urea + NBPT	0.90	y = 0.0034x-0.24	0.01

Bold P values indicate significant differences at 5% level.
CAN = Calcium Ammonium Nitrate; NBPT = N-(n-butyl) thiophosphoric triamide. MP = Moorepark; JC = Johnstown Castle; HB= Hillsborough sites.

value, and four out of 30 were observed for urea + NBPT. Thus, the use of a default value for all fertiliser N formulations is an imprecise approach, and countries should therefore endeavour to measure country-specific, fertiliser-specific and rate-specific EFs to improve their inventory accuracy of N₂O emissions. In the present study, the mean EF for CAN across rates and site-years was 1.62 % compared with 0.46 % for urea and 0.6 % for urea + NBPT. This is evidence that substantial reductions in N₂O loss can be achieved using urea-based fertilisers. Other studies in temperate grassland have also reported greater N₂O emissions from nitrate-based fertiliser formulation than the urea-based fertilisers (Dobbie and Smith, 2003; Harty et al., 2016; Watson et al., 2009) but none of these have examined the effect of N application rate. Cowan et al. (2020) stated that N₂O EFs for nitrate-based formulations were almost two times higher than those of urea-based fertiliser formulations. In the present study, the average EF for CAN was

approximately 3.5 times higher than EFs from the urea formulations, which is an important finding. Krol et al. (2020) also reported a higher annual N₂O EF from CAN (0.58 %) compared with urea (0.07 %) and urea + NBPT (0.06). Although the EFs of Krol et al. (2020), at one site-year and rate, were lower than the average of the present study, they represent a more than eightfold difference between CAN and the urea based formulations. Denitrification is a driver of N₂O production in the soil, which is dependent on soil nitrate concentration along with moisture and labile C (Butterbach-Bahl et al., 2013). Fifty percent of the N in CAN is in the form of nitrate, making it readily available for denitrification if soil conditions are suitable. In comparison, urea-based formulations must go through a number of transformations before reaching the nitrate form. Urea first undergoes hydrolysis before forming ammonium, which is subsequently nitrified to nitrate. Hydrolysis is a rapid process that occurs within several hours after urea fertiliser application in the soil. The contact of urea with soil increase ammonium content of the soil and, a localised increase in pH around the fertiliser granule results in the volatilisation loss of ammonia gas (NH₃) (Saggar et al., 2013), which is an indirect source of N₂O. Because of the NH₃ loss from urea, the net potential N source of N₂O in the soil is reduced. In the present study, on average the urea EF (0.46) was lower than that for urea + NBPT (0.6). Volatilisation loss of NH₃ gas from urea fertilisers were significantly higher than that of CAN or urea + NBPT (Dobbie and Smith, 2003; Forrester et al., 2016; Watson et al., 2000, 1990) and may explain why urea in the current study had a lower EF than urea + NBPT in 22 out of 30 comparisons (Table 3). The same result was also found in the study of Smith et al. (2012). In contrast to the results of the present study, by analysing a global dataset, Bouwman et al. (2002) stated that nitrate-based fertilisers showed lower N₂O emissions than ammonium-based formulations. Using the synthesis of another dataset, Stehfest and Bouwman (2006) concluded that in terms of N₂O emissions, there was no substantial difference between the most fertiliser types. The results of the present study are important because they do not support that finding for temperate grasslands, which is a significant land use.

The present study found that treatment of urea + NBPT (urease inhibitor) did not reduce direct N₂O emissions compared with urea. This finding supports those of Krol et al. (2020) and Harty et al. (2016), who found no significant reduction of direct N₂O emissions with urea + NBPT compared with urea alone, but instead substantial reductions when compared with CAN. However, urea with urease inhibitor NBPT has been shown to significantly reduce NH₃ emissions compared with urea alone (Watson et al., 2009, 2008), which could lead to a reduction

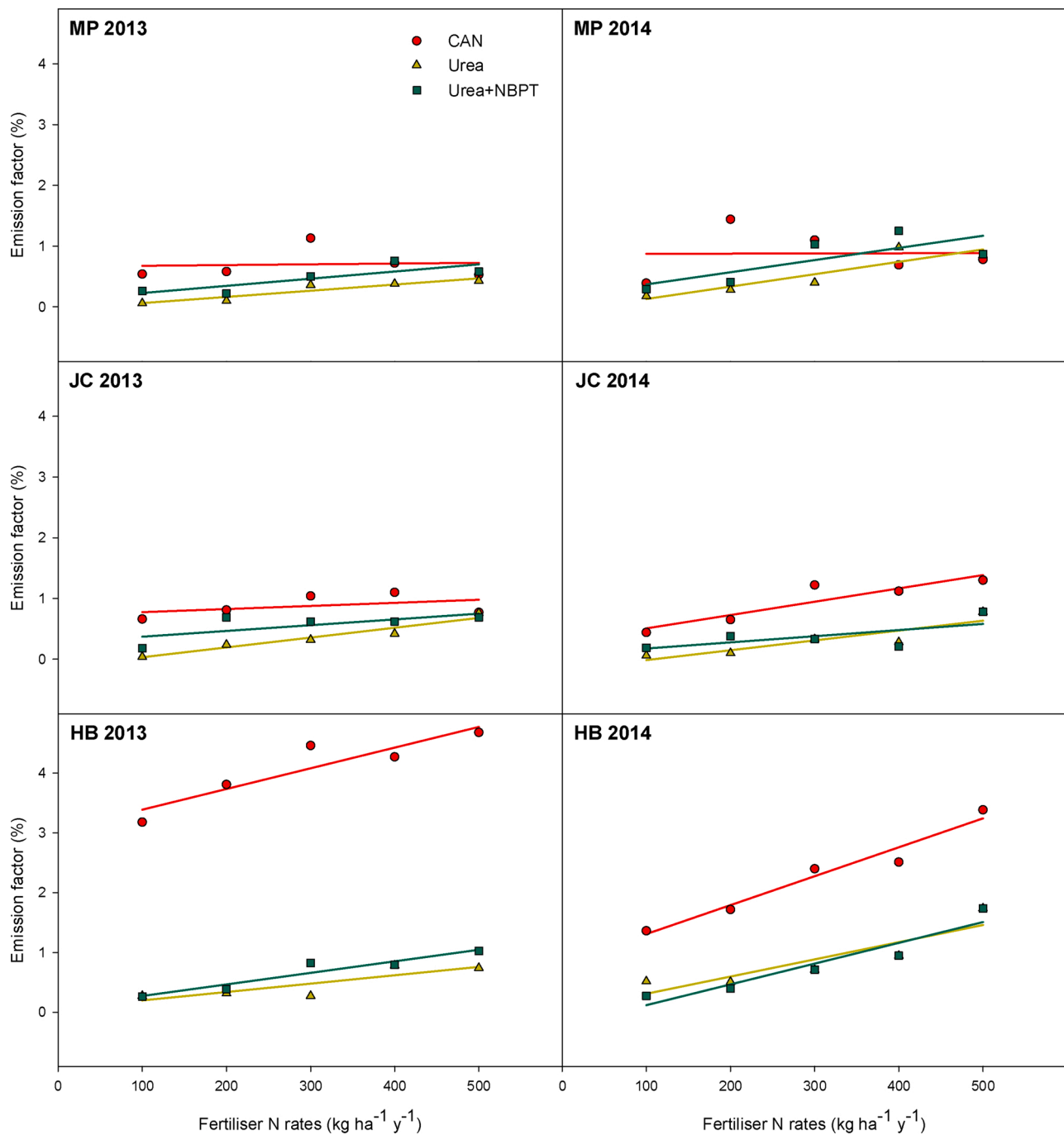


Fig. 2. Relationship between N₂O-N emission factors with five N application rates at six site-years in Ireland.

in indirect N₂O loss (Forrestal et al., 2016). In contrast to the present findings, Ding et al. (2015) reported that the use of NBPT with urea during the wheat-growing season on the North China Plain significantly reduced N₂O peak fluxes, with 50 % lower cumulative N₂O emissions than with urea, by adjusting soil nitrite intensity (Maharjan and Venterea, 2013). They argued that the application of a urease inhibitor with urea could effectively regulate nitrite concentrations, which might be more closely correlated with N₂O emissions than soil nitrate or ammonium concentrations (Zaman et al., 2009). A similar effect of urea + NBPT reducing N₂O has also been reported by Tian et al. (2015) during cotton production in the subtropical Mississippi delta region and from an unirrigated barley field in a similar region in Madrid (Abalos et al., 2012). Mazzetto et al. (2020) and Sha et al. (2020) also stated that the use of urease inhibitors resulted in a 73 and 74 % reduction in N₂O-EFs

than urea in China and Brazil, respectively. The present findings indicated that in temperate grassland soils with relatively high organic matter (source of labile C), an NBPT effect reducing direct N₂O emissions from urea is either not pronounced or completely absent.

4.2. The influence of different N fertiliser rates on N₂O emission

The results of the present study support previous studies (Bell et al., 2016; Cardenas et al., 2019, 2010; Hoben et al., 2011; Roche et al., 2016) that N fertiliser rate effects N₂O emission. The present study used a large number of rates (five) and evaluated the effect on EF, which is ultimately what will be used in inventory calculations. Not surprisingly as the annual N rate increased so too did the annual N₂O loss (Table 3). In a New Zealand pasture soil, Dai et al. (2013) also reported a positive

correlation between N application rate and N₂O emission. Thus, increasing the N supplied by the N fertilisers may increase N₂O emission by increasing the accessibility of N for the microbial performance in the soil (Dai et al., 2013; Di et al., 2010).

National inventories of GHG emissions from fertiliser calculated by Tier I and II are based on fertiliser sales, with an N₂O EF applied to the fertiliser tonnage. The EF used is either the IPCC default or a country specific value. Consequently, from an emissions inventory perspective, it is important to understand whether increasing cumulative emissions in response to increasing N fertiliser application rate has any effect on the EF. In the present study, this relationship was evaluated by testing the slope of the relationship between the N rate and the EF (Table 4). The slope was found to be positive in three, five and two sites out of six site-years for CAN, urea and urea + NBPT treatments, respectively (Fig. 2 and Table 4). These results indicate that the N rate and N₂O-N EF relationship is not consistent across site-years or across fertiliser formulations. Bell et al. (2016) found an inconsistent increase in the N₂O-EF in response to the increasing rate of the AN application in the arable croplands. Roche et al. (2016) also reported an insignificant correlation between CAN rate and the EF in spring barley cropping at one site in Ireland. But they found a significant negative relation between urea application rate and the EF which contrasts with the findings in the present grassland study. Some other studies have also reported non-consistent responses of N₂O EFs to incremental additions of N fertiliser. For example, Kim et al. (2013) reported cases of direct N₂O-N EFs remaining constant in response to increasing N application. They also reported increases and decreases in EF with changing N input. In the present study, increasing EFs in response to N application were most common for urea (five site-years) and least common for urea + NBPT (two site-years) (Fig. 2 and Table 4). No incidences of a significant negative slope were detected, indicating that decreasing N₂O EF in response to increasing N rate less likely. Direct N₂O emissions have been reported to increase sharply at the N application rates above the plant uptake capacity which ultimately influence N₂O production by preventing the biochemical reduction of N₂O emission (Kim et al., 2013). This abrupt increase in N₂O emissions was not observed within the range of N rates used in the present study, perhaps because in a parallel study grass yield has been shown to respond significantly to N rates up to 400 kg N ha⁻¹ at five out of six site-years (Forrestal et al., 2017). In the same trials, plant N uptake subsequently increased up to 500 kg N ha⁻¹ at all site-years.

4.3. Variability in N₂O emission factors across the sites

Nitrous oxide emissions exhibited substantial differences between experimental sites. This study showed a wide range of EFs for the six site-years tested across the three different fertiliser N formulations. Both CAN and urea demonstrated highly variable N₂O EFs. For these N fertilisers a coefficient of variation (cv.) of 81 % and 77 % for CAN and urea, respectively was measured over the 30 EFs generated for five N rates and six site-years. In comparison, the EFs for urea + NBPT treatments were less variable across all sites-years (cv. 59 %). The wide range of variability in EFs reported in the present study (from 0.04 – 4.68 % of the applied N) was partly due to the different climatic conditions, rainfall, temperature and management practices between the field sites (Supplementary Fig. 1). A wide range of EFs (0.44–2.86 %) has also been reported by Cardenas et al. (2019) for five rates of AN fertiliser application (from 80 – 400 kg N ha⁻¹), at five different sites in the UK. The present study also provides evidence that N₂O losses from CAN and urea fertilisers are more variable than for urea + NBPT fertiliser, when soil and environmental factors are favourable for denitrification loss as they often are in Irish temperate grasslands. Annual emissions between the six site-years varied up to 21-fold for CAN, 12 and 14-fold for urea and urea + NBPT, respectively. Dobbie and Smith (2003) also found that annually N₂O emissions from grassland can vary by up to 16-fold for AN fertiliser applications at different grassland sites in the UK due to the

variability of rainfall (timing and amount) and timing of the fertiliser application.

In the current study, all CAN treatments showed the highest EFs at the HB site, which was chosen to represent higher soil organic matter and rainfall (Table 1), which is also prevalent in Ireland (Table 3). The overall annual average EF at the HB site for the five CAN N rates (100–500 kg N ha⁻¹ yr⁻¹) was 1.33–4.68 % of total N applied (Table 3). These results suggest that if the 1 % EF is applied in such locations and the fertiliser used by farmers is CAN, N₂O fluxes will be underestimated. However, a previous study also at the HB location by Cardenas et al. (2019) reported an EF of 0.65 % for CAN applications of 400 kg N ha⁻¹ in the dry growing season of 2011. The report of Cardenas et al. (2019) is much lower than the findings at the HB site in the current study, namely 4.27 % and 2.45 % in 2013 and 2014, respectively at the application rate of 400 kg N ha⁻¹. The current study illustrates the variability of EF outcomes, particularly at the HB site where soil conditions combined with higher precipitation are conducive for denitrification of soil nitrate. The greater the water-filled pore space (WFPS), the smaller the number of soil pores filled with air, enhancing N₂O produced by denitrification. Soil moisture is also influenced by soil texture and C content of the soil. The HB soil texture was classified as a clay loam (gleysol) soil whereas, the MP and JC site represent sandy loam textured soil. In the clayey soil, the small amount of macropores increases anaerobic microsites, result in more frequent stimulation of either partial or total denitrification (depending on the soil redox potential) resulting in higher N₂O emissions from fine textured soils (Butterbach-Bahl and Gundersen, 2011). In addition, soils with higher carbon content were observed in HB sites compared to MP and JC sites (Table 1) which could increase the N₂O production by influencing nitrification and denitrification reactions (Bremner, 1997). Available C can stimulate microbial growth and activity by providing the organic carbon needed by soil denitrifiers (Cameron et al., 2013). Thus, in the present study, higher EFs at HB in 2013 may have been associated with rainfall during the experimental period, which was considerably (17 %) higher than the 30-year average for that site, fine-textured gleysol and a high amount of soil C may led to a continuously higher WFPS. Continuous saturated soil condition at the HB site in 2013 might have promoted microbial denitrifier populations, which could have also promoted the high N₂O emissions (Mancino and Torello, 1986). Moreover, fine-textured soil at this site might inhibit drainage, promoting a low oxygen condition and anaerobic microsites which favour denitrification, thus tending to promote N loss as N₂O (Dennis et al., 2012). Differences in rainfall rates during the two years at HB can explain the differences in the range of CAN EFs. The higher CAN EF ranges in 2013 than in 2014 were the result of higher rainfall during the former. Rafique et al. (2011) also found a different range of EFs (1.14–3.07 %) at different grassland sites in southern Ireland, which were mostly dependent on the application of N fertiliser, variations in soil type, temperature, rainfall and grazing management.

Yearly rainfall and temperature values during the experimental period were comparable to the long-term values at all sites, signifying that the climatic conditions were representative of a typical year. This highlights that the N₂O-N EFs reported are representative of the levels of loss to be expected for these individual fertiliser formulations applied in Ireland, with the potential for emissions to be refined in accordance with soil and weather conditions.

4.4. The suitability of using a single emission factor across N formulations and rates

For accurate GHG accounting, countries are moving from tier I to tier II country-specific EF based on each formulation (single value) across all the N rates. The question remains if countries can adequately capture N₂O emissions for each fertiliser formulation by using a generalised single EF across all N rates and is that approach good enough for accurately capturing the GHG budget? Firstly, it is evident from our results that the use of a single universal EF across all N formulations is

not appropriate and that efforts should be made to produce country specific EFs for N formulations on an individual basis. The present study provides this information for Irish temperate grasslands and gives insight for other temperate grasslands. In terms of the effect of N rate on EF the picture is more complex. For CAN in three out of six site-years (or 50 % of the cases) the slope of the relationship between N rate and EF increased significantly (Table 4). For urea, NBPT appeared to play a role with a positive slope in EF in response to increasing N rate detected in only two (33 % of cases) out of six site-years compared to five out of six-years (83 % of cases) for urea. Our finding indicates that although urea always had a lower EF than CAN the urea EF was more sensitive to increasing N rate than that of CAN. Many studies have examined the linearity/non-linearity of N₂O fluxes or EFs (Cardenas et al., 2019; Hoben et al., 2011; Kim et al., 2013; McSwiney and Robertson, 2005) indicating/finding conflicting results. Few studies have examined the slope of the relationship between N rate and EF, or had the large number of rates needed to do this effectively, as has been done in the present study. This relationship is particularly important for the calculation of national inventories of emission in situations where the activity data on N rate is available. More work is needed to understand why the EFs with urea + NBPT are relatively unaffected by N rate compared with standard urea. Thus from our results, it is clear that there is a need for countries to move towards inventory approaches which capture both N formulation, N rate and soil conditions. National activity data concerning fertiliser type, application rates and soils should also be a focus.

5. Conclusions

The current study found significant differences between fertilisers and in the effect of rate on N₂O emissions and EFs which can inform the development of loss mitigation strategies, farm and policy decisions. The current study showed that by a factor of more than three, urea based formulations had a lower direct N₂O loss (mean 0.46 urea; 0.6 urea + NBPT) compared to CAN (mean 1.62) in these temperate grasslands. This information opens the opportunity for N formulation selection to provide a tool to alter N₂O loss outcomes at the farm scale. Such considerations should also consider other N loss pathways such as ammonia volatilisation of urea, for example, which makes urea + NBPT the preferred option. Additionally, increasing N rate increased absolute N₂O loss for all fertilisers. However, the impact of increasing N application on the EF was not consistent across fertilisers. This is also important for GHG inventory calculations which often assumes a fixed EF across N applied regardless of rate. The current study demonstrates that the slope of the relationship between N rate and EF is generally positive for urea (5 of 6 site-years). Whereas for CAN the picture is less clear with N rate significantly increasing the EF in only 50 % of site-years. There is strong evidence to move away from the IPCC default value of 1 % to fertiliser-specific EFs. Furthermore, capturing the effect of rate and site characteristics provides a pathway towards refined national GHG inventories. The challenge for the fertiliser industry into the future is to produce a generation of N fertilisers that perform strongly when confronted with all N loss pathways across the diverse conditions in which they are applied. To do so, all tools should be considered since the requirement for N by many plants, places constraints on the capacity to reduce N without incurring a yield penalty or markedly changing the system.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

The authors would like to thank the laboratory and field staff at Teagasc Johnstown Castle, Teagasc Moorepark, Agri-Food and Biosciences Institute with their assistance on this project. This research was financially supported under the National Development Plan, through the

Research Stimulus Fund, administered by the Department of Agriculture, Food and the Marine (Grant numbers RSF10-/RD/SC/716 and RSF11S138), Ireland and from the Department of Agriculture, Environment and Rural Affairs (Ref: DAERA, Evidence and Innovation project 13/04/06) for Northern Ireland.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.agee.2021.107382>.

References

- Abalos, D., Sanz-Cobena, A., Misselbrook, T., Vallejo, A., 2012. Effectiveness of urease inhibition on the abatement of ammonia, nitrous oxide and nitric oxide emissions in a non-irrigated Mediterranean barley field. *Chemosphere* 89 (3), 310–318.
- Bell, M.J., Cloy, J.M., Topp, C.F.E., Ball, B.C., Bagnall, A., Rees, R.M., Chadwick, D.R., 2016. Quantifying N₂O emissions from intensive grassland production: the role of synthetic fertiliser type, application rate, timing and nitrification inhibitors. *J. Agric. Sci.* 154 (5), 812–827.
- Bouwman, A.F., Boumans, L.J.M., Batjes, N.H., 2002. Emissions of N₂O and NO from fertilised fields: Summary of available measurement data. *Global Biogeochem. Cycles* 16 (4), 6–1.
- Butterbach-Bahl, K., Gundersen, P., 2011. In: Sutton, Mark A., Cl, Howard, Erisman, Jan Willem, Billen, Gilles, Bleeker, Albert, Grennfelt, Peringe, Grinsven, Hansvan, Grizzetti, Bruna (Eds.), *Nitrogen Processes in Terrestrial Ecosystems in the European Nitrogen Assessment*. Cambridge University Press, Cambridge, UK. Available at: <http://hdl.handle.net/1854/LU-2042092>. (Accessed 01/02/2021).
- Bremner, J.M., 1997. Sources of nitrous oxide in soils. *Nutr. Cycling Agroecosyst.* 49 (1), 7–16. <https://doi.org/10.1023/A:1009798022569>.
- Butterbach-Bahl, K., Baggs, E.M., Dannenmann, M., Kiese, R., Zechmeister-Boltenstern, S., 2013. Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Philos. Trans. R. Soc. B* 368 (1621), 20130122.
- Cardenas, L.M., Thorman, R., Ashlee, N., Butler, M., Chadwick, D., Chambers, B., Cuttle, S., Donovan, N., Kingston, H., Lane, S., Dhanoa, M.S., 2010. Quantifying annual N₂O emission fluxes from grazed grassland under a range of inorganic fertiliser nitrogen inputs. *Agric. Ecosyst. Environ.* 136 (3–4), 218–226.
- Cameron, K.C., Di, H.J., Moir, J.L., 2013. Nitrogen losses from the soil/plant system: a review. *Ann. Appl. Biol.* 162 (2), 145–173.
- Cardenas, L.M., Bhogal, A., Chadwick, D.R., McGeough, K., Misselbrook, T., Rees, R.M., Thorman, R.E., Watson, C.J., Williams, J.R., Smith, K.A., Calvet, S., 2019. Nitrogen use efficiency and nitrous oxide emissions from five UK fertilised grasslands. *Sci. Total Environ.* 661, 696–710.
- Chadwick, D.R., Cardenas, L., Misselbrook, T.H., Smith, K.A., Rees, R.M., Watson, C.J., McGeough, K.L., Williams, J.R., Cloy, J.M., Thorman, R.E., Dhanoa, M.S., 2014. Optimising chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments. *Eur. J. Soil Sci.* 65 (2), 295–307.
- Clayton, H., McTaggart, I.P., Parker, J., Swan, L., Smith, K.A., 1997. Nitrous oxide emissions from fertilised grassland: a 2-year study of the effects of N fertiliser form and environmental conditions. *Biol. Fertil. Soils* 25 (3), 252–260.
- Cowan, N., Carnell, E., Skiba, U., Dragosits, U., Drewer, J., Levy, P., 2020. Nitrous oxide emission factors of mineral fertilisers in the UK and Ireland: a Bayesian analysis of 20 years of experimental data. *Environ. Int.* 135, 105366.
- CSO, 2018. *Statistical Yearbook of Ireland 2017*. Central Statistics Office. Farm Structure Survey – Survey Coverage. <http://www.cso.ie/en/media/csoie/releasespublications/documents/statisticalyearbook/2012/c10agriculture.pdf>.
- DAFM, 2019. 'Ag-Climate' – A Draft National Climate & Air Roadmap for the Agriculture Sector to 2030 and Beyond – Public Consultation. Department of Agriculture, Food and the Marine, Ireland.
- Dai, Y., Di, H.J., Cameron, K.C., He, J.Z., 2013. Effects of nitrogen application rate and a nitrification inhibitor dicyandiamide on ammonia oxidisers and N₂O emissions in a grazed pasture soil. *Sci. Total Environ.* 465, 125–135. <https://doi.org/10.1016/j.scitotenv.2012.08.091>.
- de Klein, C.A.M., Harvey, M. (Eds.), 2012. *Nitrous Oxide Chamber Methodology Guidelines*. Ministry for Primary Industries, New Zealand. Available at: <http://www.globalresearchalliance.org/research/livestock/activities/nitrous-oxide-chamber-methodology-guidelines/>. (Accessed: 28/6/2020).
- Dennis, S.J., Cameron, K.C., Di, H.J., Moir, J.L., Staples, V., Sills, P., Richards, K.G., 2012. Reducing nitrate losses from simulated grazing on grassland lysimeters in Ireland using a nitrification inhibitor (dicyandiamide). In: *Biology and Environment: Proceedings of the Royal Irish Academy*. Royal Irish Academy, pp. 79–89.
- Di, H.J., Cameron, K.C., Sherlock, R.R., Shen, J.P., He, J.Z., Winefield, C.S., 2010. Nitrous oxide emissions from grazed grassland as affected by a nitrification inhibitor, dicyandiamide, and relationships with ammonia-oxidising bacteria and archaea. *J. Soils Sediments* 10 (5), 943–954.
- Ding, W.X., Chen, Z.M., Yu, H.Y., Luo, J.F., Yoo, G.Y., Xiang, J., Yuan, J.J., 2015. Nitrous oxide emission and nitrogen use efficiency in response to nitrophosphate, N-(n-butyl) thiophosphoric triamide and dicyandiamide of a wheat cultivated soil under sub-humid monsoon conditions. *Biogeosciences* 12 (3).
- Dobbie, K.E., Smith, K.A., 2003. Nitrous oxide emission factors for agricultural soils in Great Britain: the impact of soil water-filled pore space and other controlling variables. *Glob. Change Biol.* 9 (2), 204–218.

- EC, 2018. Final Report of the High-Level Panel of the European Decarbonisation Pathways Initiative. European Commission. Available at: <https://ec.europa.eu/info/sites/info/files/rec-18-002-decarbonisation-booklet-27112018.pdf>, (Accessed 24/02/2020).
- Emmet-Booth, J.P., Dekker, S., O'Brien, P., 2019. Climate Change Mitigation and the Irish Agriculture and Land Use Sector. Working paper on Climate Change Advisory Council. Dublin, Ireland. Available at: <http://www.climatecouncil.ie/media/WorkingPaper%20on%20Agriculture%20and%20Land%20Use.pdf> (Accessed 04/02/2020).
- FAO/STAT, 2017. Food and Agriculture Organization of the United Nations. Statistical Division. [WWW Document]. Available at <http://faostat3.fao.org/home/E> (Accessed: 18/06/2019).
- Forrestal, P.J., Harty, M., Carolan, R., Lanigan, G.J., Watson, C.J., Laughlin, R.J., McNeill, G., Chambers, B.J., Richards, K.G., 2016. Ammonia emissions from urea, stabilised urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland. *Soil Use Manag.* 32, 92–100.
- Forrestal, P.J., Harty, M.A., Carolan, R., Watson, C.J., Lanigan, G.J., Wall, D.P., Richards, K.G., 2017. Can the agronomic performance of urea equal calcium ammonium nitrate across nitrogen rates in temperate grassland? *Soil Use Manag.* 33 (2), 243–251.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. Changes in atmospheric constituents and in radiative forcing. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK/New York, NY, USA.
- Garwood, E.A., Ryden, J.C., 1986. Nitrate loss through leaching and surface runoff from grassland: effects of water supply, soil type and management. *Nitrogen Fluxes in Intensive Grassland Systems*. Springer, Dordrecht, pp. 99–113.
- Good, A.G., Beatty, P.H., 2011. Fertilising nature: a tragedy of excess in the commons. *PLoS Biol.* 9 (8), e1001124.
- Hansen, S., Bernard, M.E., Rochette, P., Whalen, J.K., Dörsch, P., 2014. Nitrous oxide emissions from a fertile grassland in Western Norway following the application of inorganic and organic fertilisers. *Nutr. Cycl. Agroecosyst.* 98 (1), 71–85.
- Harty, M.A., Forrestal, P.J., Watson, C.J., McGeough, K.L., Carolan, R., Elliot, C., Krol, D., Laughlin, R.J., Richards, K.G., Lanigan, G.J., 2016. Reducing nitrous oxide emissions by changing N fertiliser use from calcium ammonium nitrate (CAN) to urea based formulations. *Sci. Total Environ.* 563, 576–586.
- Hinton, N.J., Cloy, J.M., Bell, M.J., Chadwick, D.R., Topp, C.F.E., Rees, R.M., 2015. Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated Cambisol in Scotland. *Geoderma Reg.* 4, 55–65.
- Hoben, J.P., Gehl, R.J., Millar, N., Grace, P.R., Robertson, G.P., 2011. Non-linear nitrous oxide (N₂O) response to nitrogen fertiliser in on-farm corn crops of the US Midwest. *Glob. Change Biol.* 17 (2), 1140–1152.
- Hyde, B.P., Hawkins, M.J., Fanning, A.F., Noonan, D., Ryan, M., O'toole, P., Carton, O.T., 2006. Nitrous oxide emissions from a fertilised and grazed grassland in the South East of Ireland. *Nutr. Cycl. Agroecosyst.* 75 (1–3), 187–200.
- IPCC, 2006. Guidelines for National Greenhouse Gas Inventories, Agriculture, Forestry and Other Land Use. Chapter 11: N₂O Emissions from Managed Soils, and CO₂ Emissions from Lime and Urea Application. Intergovernmental Panel on Climate Change (IPCC), Vol. 4. Institute for Global Environmental Strategies, Tokyo, Japan, 2006.
- IPCC, 2013. Anthropogenic and natural radiative forcing. In: Stocker, T.F., Qin, D., Plattner, G.K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), *Climate Change 2013: The Physical Science Basis*. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Jones, S.K., Rees, R.M., Skiba, U.M., Ball, B.C., 2005. Greenhouse gas emissions from a managed grassland. *Glob. Planet. Change* 47 (2–4), 201–211.
- Kelliher, F.M., Sherlock, R., Clough, T.J., Premaratne, M., Laughlin, R.J., McGeough, K.L., Harvey, M.J., McMillan, A.M.S., Reid, A., Saggart, S., 2013. Air sample collection, storage and analysis. In: de Klein, C.A.M., Harvey, M.J. (Eds.), *Nitrous Oxide Chamber Methodology Guidelines*, Version 1.0, Chapter 4, Global Research Alliance on Agricultural Greenhouse Gases. Ministry for Primary Industries, New Zealand.
- Kim, D., Hernandez-Ramirez, G., 2010. Dependency of nitrous oxide emission factors on nitrogen input rates: a meta-analysis. In: *Proceedings 19th World Congress of Soil Science*. Greenhouse Gases from Soils, IUSS, Brisbane, Congress Symposium, Vol. 4, pp. 40–43.
- Kim, D.G., Hernandez-Ramirez, G., Giltrap, D., 2013. Linear and non-linear dependency of direct nitrous oxide emissions on fertiliser nitrogen input: a meta-analysis. *Agric. Ecosyst. Environ.* 168, 53–65.
- Krol, D.J., Forrestal, P.J., Wall, D., Lanigan, G.J., Sanz-Gomez, J., Richards, K.G., 2020. Nitrogen fertilisers with urease inhibitors reduce nitrous oxide and ammonia losses, while retaining yield in temperate grassland. *Sci. Total Environ.*, 138329
- Maharjan, B., Venterea, R.T., 2013. Nitrite intensity explains N management effects on N₂O emissions in maize. *Soil Biol. Biochem.* 66, 229–238.
- Mancino, C.F., Torello, W.A., 1986. Enumeration of denitrifying microbial populations in turf. *Plant Soil* 96 (1), 149–151.
- Mazzetto, A.M., Styles, D., Gibbons, J., Arndt, C., Misselbrook, T., Chadwick, D., 2020. Region-specific emission factors for Brazil increase the estimate of nitrous oxide emissions from nitrogen fertiliser application by 21%. *Atmos. Environ.*, 117506
- McSwiney, C.P., Robertson, G.P., 2005. Non-linear response of N₂O flux to incremental fertiliser addition in a continuous maize (*Zea mays* L.) cropping system. *Glob. Change Biol.* 11 (10), 1712–1719.
- O'Mara, F.P., 2012. The role of grasslands in food security and climate change. *Ann. Bot.* 110 (6), 1263–1270.
- Rafique, R., Hennessy, D., Kiely, G., 2011. Nitrous oxide emission from grazed grassland under different management systems. *Ecosystems* 14 (4), 563–582.
- Rahman, N., Bruun, T.B., Giller, K.E., Magid, J., van de Ven, G.W., de Neergaard, A., 2019. Soil greenhouse gas emissions from inorganic fertilizers and recycled oil palm waste products from Indonesian oil palm plantations. *GCB Bioenergy* 11 (9), 1056–1074.
- Ravishankara, A.R., Daniel, J.S., Portmann, R.W., 2009. Nitrous oxide (N₂O): the dominant ozone-depleting substance emitted in the 21st century. *Science* 326 (5949), 123–125.
- Reay, D.S., Davidson, E.A., Smith, K.A., Smith, P., Melillo, J.M., Dentener, F., Crutzen, P. J., 2012. Global agriculture and nitrous oxide emissions. *Nat. Clim. Change* 2 (6), 410–416.
- Rees, R.M., Augustin, J., Alberti, G., Ball, B.C., Boeckx, P., Cantarel, A., Castaldi, S., Chirinda, N., Chojnicki, B., Giebels, M., Gordon, H., 2013. Nitrous oxide emissions from European agriculture: an analysis of variability and drivers of emissions from field experiments. *Biogeosciences* 10 (4), 2671–2682.
- Reeves, S., Wang, W., 2015. Optimum sampling time and frequency for measuring N₂O emissions from a rain-fed cereal cropping system. *Sci. Total Environ.* 530, 219–226.
- Roche, L., Forrestal, P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J., Wall, D.P., 2016. Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. *Agric. Ecosyst. Environ.* 233, 229–237.
- Saggart, S., Singh, J., Giltrap, D.L., Zaman, M., Luo, J., Rollo, M., Van der Weerden, T.J., 2013. Quantification of reductions in ammonia emissions from fertiliser urea and animal urine in grazed pastures with urease inhibitors for agriculture inventory: New Zealand as a case study. *Sci. Total Environ.* 465, 136–146.
- Sha, Z., Ma, X., Loick, N., Lv, T., Cardenas, L.M., Ma, Y., Misselbrook, T., 2020. Nitrogen stabilisers mitigate reactive N and greenhouse gas emissions from an arable soil in North China Plain: field and laboratory investigation. *J. Clean. Prod.*, 121025
- Smith, K.A., Dobbie, K.E., Thorman, R., Watson, C.J., Chadwick, D.R., Yamulki, S., Ball, B.C., 2012. The effect of N fertiliser forms on nitrous oxide emissions from UK arable land and grassland. *Nutr. Cycl. Agroecosyst.* 93 (2), 127–149.
- Stehfest, E., Bouwman, L., 2006. N₂O and NO emission from agricultural fields and soils under natural vegetation: summarising available measurement data and modeling of global annual emissions. *Nutr. Cycl. Agroecosyst.* 74 (3), 207–228.
- Tian, Z., Wang, J.J., Liu, S., Zhang, Z., Dodla, S.K., Myers, G., 2015. Application effects of coated urea and urease and nitrification inhibitors on ammonia and greenhouse gas emissions from a subtropical cotton field of the Mississippi delta region. *Sci. Total Environ.* 533, 329–338.
- Watson, C.J., 2000. Urease activity and inhibition - principles and practice. *Proceedings - International Fertiliser Society* 2000. No. 454 1–40. ISSN1466-1314.
- Watson, C.J., Stevens, R.J., Laughlin, R.J., 1990. Effectiveness of the urease inhibitor NBPT (N-(n-butyl) thiophosphoric triamide) for improving the efficiency of urea for ryegrass production. *Fert. Res.* 24 (1), 11–15.
- Watson, C.J., Akhonzada, N.A., Hamilton, J.T.G., Matthews, D.I., 2008. Rate and mode of application of the urease inhibitor N-(n-butyl) thiophosphoric triamide on ammonia volatilisation from surface-applied urea. *Soil Use Manag.* 24, 246–253.
- Watson, C.J., Laughlin, R.J., McGeough, K.L., 2009. Modification of nitrogen fertilisers using inhibitors: opportunities and potentials for improving nitrogen use efficiency. In: *Proceedings-International Fertiliser Society* (No. 658). International Fertiliser Society, pp. 1–40. ISSN1466-1314.
- Zaman, M., Saggart, S., Blennerhassett, J.D., Singh, J., 2009. Effect of urease and nitrification inhibitors on N transformation, gaseous emissions of ammonia and nitrous oxide, pasture yield and N uptake in grazed pasture system. *Soil Biol. Biochem.* 41, 1270–1280.