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TITLE: Reducing nitrous oxide emissions by changing N fertiliser use from calcium ammonium nitrate (CAN) to urea based formulations.

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Highlights

- The N_2O emission factor for CAN was substantially higher than the IPCC default and highly variable between sites and across years.

- Urea products decreased direct N_2O emissions from CAN on average by 80%

- Switching from CAN to urea products reduces both N_2O emissions and fertiliser costs.

Abstract

The accelerating use of synthetic nitrogen (N) fertilisers, to meet the world's growing food demand, is the primary driver for increased atmospheric concentrations of nitrous oxide (N_2O). The IPCC default emission factor (EF) for N_2O from soils is 1% of the N applied, irrespective of its form. However, N_2O emissions tend to be higher from nitrate-containing fertilisers e.g. calcium ammonium nitrate (CAN) compared to urea, particularly in regions, which have mild, wet climates and high organic matter soils. Urea can be an inefficient N source due to NH_3 volatilisation, but nitrogen stabilisers (urease and nitrification inhibitors) can improve its efficacy. This study evaluated the impact of switching fertiliser formulation from calcium ammonium nitrate (CAN) to urea-based products, as a potential mitigation strategy to reduce N_2O emissions at six temperate grassland sites on the island of Ireland. The surface applied formulations included CAN, urea and urea with the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) and/or the nitrification inhibitor dicyandiamide (DCD). Results showed that N_2O emissions were significantly affected by fertiliser formulation, soil type and climatic conditions. The direct N_2O emission factor (EF) from CAN averaged 1.49% overall sites, but was highly variable, ranging from 0.58% to 3.81. Amending urea with NBPT, to reduce ammonia volatilisation, resulted in an average EF of 0.40% (ranging from 0.21 to 0.69%)-compared to an average EF of 0.25% for urea (ranging from 0.1 to 0.49%), with both fertilisers significantly lower and less variable than CAN. Cumulative N_2O emissions from urea amended with both NBPT and DCD were not significantly different from background levels. Switching from CAN to stabilised urea formulations was found to be an effective strategy to reduce N_2O emissions, particularly in wet, temperate grassland.

Key words nitrous oxide mitigation; emission factor; calcium ammonium nitrate; stabilised urea; nitrification inhibitor Dicyandiamide (DCD); urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT).

1. Introduction

Agriculture, incorporating forestry, and other land uses (AFOLU), is estimated to be responsible for just under a quarter of anthropogenic greenhouse gas (GHG) emissions (IPCC, 2014) with food production estimated to be responsible for generating 60% of anthropogenic nitrous oxide (N_2O) emissions in 2006 (Syakila and Kroeze, 2011). The primary driver for increased concentrations of N_2O is enhanced microbial activity in highly fertilised agricultural lands (IPCC, 2007), with the accelerating use of synthetic nitrogen (N) fertilisers driving this increase since the 1960s (Davidson, 2009). N_2O emissions in temperate grasslands are associated with the application of organic or inorganic N inputs. These inputs increase the size of the ammonium (NH_4^+)-N and nitrate (NO_3^-)-N pools in the soil which are in turn subject to a variety of biotic and abiotic processes which ultimately generate N_2O. The two most important processes are nitrification, (the oxidation of NH_4^+ to NO_2^- and NO_3^-) and biological denitrification, the process by which NO_3^- is reduced to the gaseous compounds, NO, N_2O and N_2 (Meixner and Yang, 2006). Optimal conditions for denitrification include high soil water filled pore space (WFPS), combined with sufficient NO_3^- and an available carbon (C) source (Davidson and Swank, 1986; Davidson et al., 2000; Shelton et al., 2000).

1.1 N_2O sources

In Europe, grassland is one of the dominant land uses, and the major contributor to greenhouse gas emissions, with fluxes closely associated with management practices (Soussana et al., 2007). In 2011, about 38% of European agricultural land was devoted to permanent grassland (FAOSTAT, 2015); while in Ireland, in the same year, this figure was over 82% (for improved grassland) increasing to 92% upon inclusion of rough grazing (CSO, 2012). Quantification of N_2O emissions is challenging due to a large number of interacting drivers that result in a high degree of temporal and spatial heterogeneity in emissions, which

are generally characterised by "hot spots and hot moments" (Butterbach-Bahl et al., 2013). In grassland soils high levels of soil microbial activity stimulated by high C and N inputs, dense root systems and C/N input from above-ground decaying biomass are the most likely cause for high N_2O emissions (Schaufler et al., 2010).

1.2 Fertiliser form

Globally consumption of straight N products is 137.7 Mt N yr^{-1} of which 63% is urea and 10% is ammonium nitrate/calcium ammonium nitrate (AN/CAN). In contrast, N consumption in Western Europe is dominated by AN/CAN. In the UK N consumption is 0.86 Mt N yr^{-1} of which 64% is AN/CAN and only 18.3% urea (IFADATA, 2013). In Ireland, CAN and urea application on grassland is in the ratio of 84:16 (Duffy et al., 2014). The reasons for the relatively low urea usage across the UK and Ireland goes back to results from early experiments which showed that urea was less effective than other straight forms of N (Smil, 2001). This was often due to a) loss of N efficiency due to ammonia volatilisation, driven by both soil conditions and climatic factors post-fertiliser application (Watson, 2000) and b) the lower density of urea compared to AN/CAN impacting on uniform field spreading (Dampney et al., 2003).

1.3 N stabilisation

N stabilisers are compounds that extend the time the N component of the fertiliser remains in the soil in the urea or ammoniacal form (Watson et al., 2009). Natural suppression of soil nitrification by plants has also been observed in some ecosystems, and is referred to as biological nitrification inhibition (Subbarao et al., 2006). This natural inhibition is most likely an evolutionary adaptation to ensure conservation and efficient use of N in natural systems

which have low-N availability (Lata et al., 2004). There are two main categories of commercially available N stabilisers:

1.3.1 Nitrification inhibitors (NIs) are compounds that delay the bacterial oxidation of NH_4^+ by impeding the activities of soil-nitrifying bacteria (Subbarao et al., 2012). By retaining N in (NH_4^+)-N ammonium form for longer, NIs reduce losses through denitrification and leaching of NO_3^--N and potentially increase the efficiency of N applied. Dicyandiamide (DCD) has been used in agriculture for many years (Fox and Bandel, 1986) because it is cheap, soluble in water and not volatile. Although the percentage reductions in NO_3^--N leaching and N_2O emissions by DCD in New Zealand are relatively large, the additional N available for plant uptake in the soil where DCD is present is small (Smith et al., 2008, Monaghan et al., 2009).

1.3.2 Urease inhibitors (UIs) The most common commercially available urease inhibitor is Agrotain®, which was introduced onto the US market in the mid 1990's, has the active ingredient N-(n-butyl) thiophosphoric triamide (NBPT), a structural analogue of urea. The oxygen analog of NBPT (NBPTo) (Engel et al., 2015) inhibits the hydrolytic action of soil urease, which catalyses the hydrolysis of urea to ammonium carbonate, by blocking the active site of the enzyme. NBPT delays the rate of urea hydrolysis to NH_4^+-N and hence moderates the localised zones of high pH and NH_4^+-N concentrations, which result from urea hydrolysis and which are conducive to NH_3 volatilisation. The urease inhibitor has been shown to be highly effective at low concentrations (<500 ppm by weight of urea), lowering NH_3 losses from surface-applied urea (Watson et al., 2008) and increasing yield and N uptake compared with unamended urea (Watson et al., 2009). In the UK, field trials on grassland and tillage land showed that NBPT reduced ammonia emissions from untreated granular urea by 73% on average when used at a concentration of 500 or 1000 mg kg^{-1} (Chambers and Dampney, 2009). In New Zealand, the addition of NBPT increased total pasture production by 17% compared to urea alone (Zaman et al., 2008).

In addition a maleic and itaconic acid copolymer (MIP) has been marketed globally as a urease and a nitrification inhibitor under the trade name Nutrisphere®. There is limited information regarding its effect on N_2O emissions.

1.4 Impact of N form on N_2O emission factors

Meta-analyses of fertiliser types indicate that there can be differences in N_2O emissions between different fertiliser N forms (Bouwman et al., 2002; Venterea et al., 2005), with N_2O loss occurring more quickly for AN/CAN and higher N_2O emission factors (%) for AN/CAN compared to urea (Clayton et al., 1997, Dobbie and Smith 2003, Jones et al., 2007). Consequently, the portion of N delivered as NH_4^+ and NO_3^- and urea may affect N_2O emissions. Superimposed on this variation are the further impacts associated with soil type such as differences in physical characteristics, such as texture and bulk density (which impact WFPS), chemical characteristics such as soil C, N and pH, and biological properties such as the proportion of fungi and bacteria (van der Weerden et al., 2012, Kelliher et al., 2014). Despite this multiplicity of influences on N_2O emissions, the IPCC uses the same 1% default emission factor irrespective of form of N or soil type. The use of CAN, particularly at wet and/or high organic matter sites can result in high N_2O emissions (Watson et al., 2009). The rationale for the current study was to evaluate whether substituting CAN with a urea-based product could be a potential mitigation strategy to reduce direct N_2O emissions from contrasting temperate grassland soils. However, urea is subject to N loss via ammonia volatilisation and this can be mitigated by the use of a urease inhibitor and nitrification can be delayed by use of a nitrification inhibitor. An additional objective was to generate disaggregated emission factors based on N form and drainage class for inclusion in the Irish GHG Inventory.

2. Material and Methods

The experiment was conducted over two years at six permanent pasture sites at three locations on the island of Ireland: Johnstown Castle, Co. Wexford (JC) 52°18'27N, 6°30'14W, Moorepark, Co. Cork (MP) 52°9'27"N, 8°14'42"W and Hillsborough, Co. Down (HB) 54°27'827N, 6°04'57873W covering a range of soil and climatic conditions. In the second year the experiment moved to a new site at each location, to overcome any carryover effects from the first year. Both HB sites were under pasture for more than 20 years, the MP sites had been reseeded three (2013 site) and four (2014 site) years prior to the start of the experiment and the JC sites had been reseeded three years prior to (2013 site) and in the year before (2014 site) the start of the experiment. In all experimental treatments annual fertiliser N was surface applied at 200 kg N ha^{-1} in five equal splits. The experimental plots (each plot was 12m x 2m) were arranged in a randomised block design with five replicates. The treatments were:

- CAN, Urea, Urea+NBPT, Urea +DCD, Urea + NBPT + DCD and a control (zero N).

Two additional treatments were applied at the MP and JC sites in year 2.

- Urea + MIP and a CAN/urea blend (50% CAN-N and 50% Urea-N).

The same source of urea (Koch, U.S.A.) was used for all urea formulations across all sites and years (except Urea+MIP) and the DCD was incorporated into the urea melt as part of the manufacturing process, at a rate of 1.6% on a urea weight basis, giving a DCD rate of 1.39 kg DCD ha^{-1} application^{-1} or 6.96 kg DCD ha^{-1} yr^{-1}. The NBPT was coated onto the urea granule at the Agri-Food and Biosciences Institute, Belfast at a rate of 600ppm NBPT on a urea weight basis. The Urea+MIP was a commercially available product purchased for the study.

2.1 N_2O measurement and sample analysis

N_2O fluxes were measured over a 12 month period using the closed, static chamber technique (Chadwick et al., 2014) with the chamber design consistent across the three sites. The

stainless steel chambers consisted of a chamber base measuring 0.4m x 0.4m wide and 0.1m high which was inserted into the ground to a depth of ≥5 cm, with a corresponding lid of height 0.1m. The bases were inserted into the ground at least 3 days prior to commencing the experiment and were left in position for the duration of the experiment and removed only for grass harvest being returned immediately to the same position. Gas sampling was undertaken between 10.00 and 14.00 hours, as this was reported to best represent the average daily flux (Smith and Dobbie, 2001; van der Weerden et al., 2013). Reeves and Wang, (2015) refined the optimum sampling time to between mid-morning (09:00) and midday (12:00) as sampling conducted in the early afternoon was observed to overestimate daily emissions due to higher soil temperatures. Headspace samples (20 ml at HB, 10 ml at JC and MP) were taken after a 40 min chamber closure period on four occasions per week during the first and second week after N application, reducing to twice per week for the next two weeks and then once per week until the next N application. Sampling was reduced to fortnightly over the winter period, once N_2O fluxes returned to baseline levels. Two chambers per plot were used at HB and one chamber per plot was used at MP and JC. These chambers were located at one end of the experimental plots, with the remaining area being used for an agronomic trial which ran concurrently.

Ambient air samples acted as the time zero (T_0) N_2O estimate for all headspace N_2O calculations, as per Chadwick et al. (2014) who showed that using ambient air as a surrogate for individual chamber T_0 headspace samples did not result in any consistent bias in calculating fluxes. Gas samples were injected into 12 ml (HB) or 7 ml (JC and MP) pre-evacuated glass vials with double-wadded PTFE/silicone septa (Labco, UK) which were over pressurised during storage. The vials were brought back to atmospheric pressure immediately prior to analysis by gas chromatography (GC). Gas standard samples were stored and

analysed with each batch of field generated samples to determine if losses occurred during storage. GC analysis was generally completed within 2 weeks of field measurements.

The linearity (or lack of linearity) of N_2O accumulation within the chamber headspace was determined on every sampling occasion from three chambers at HB and five chambers each at MP and JC selected at random from plots receiving fertiliser. The linearity headspace gas sample was taken at 0, 15, 30, 40 and 60 minutes after lid closure for this subset of chambers. JC and MP samples were analysed for N_2O concentrations using Bruker Scion 456 GCs with a 63Ni electron capture detector (ECD) and at HB using a Bruker 450 GC-ECD (Bruker, Germany). Samples were injected into each GC using a Combi-PAL xt® auto–sampler (CTC Analytics AG, Switzerland). The precision limits for each site were calculated (Ellison et al., 2009) using the N_2O concentration of the ten ambient samples taken at each sampling event and were 44, 46 and 18 ppb for JC, MP and HB, respectively. Using site specific chamber dimensions this equated to a minimum detectable flux of 3.48, 4.00 and 1.50 g N_2O-N ha^{-1} d^{-1} for JC, MP and HB, respectively.

2.2 Calculation of N_2O emissions

2.2.1 Direct emissions

Daily fluxes (F (daily) in g N_2O-N h^{-1} d^{-1}) were calculated for each treatment from the increase in headspace concentration from the initial N_2O chamber concentration (T_0) (average of ambient) to the final N_2O chamber concentration (taken at T_{40} min after enclosure) following Eq. (1) (adapted from Kelliher et al. (2013):

$$F(daily) = (\Delta C/\Delta t) \times ((M \times P)/(R \times T)) \times (V/A) \qquad (1)$$

Where:

$\Delta C/\Delta t$ is the slope of the line for T_0 and T_{40} (Saggar et al., 2007), ΔC is the change in gas concentration in the chamber headspace during the enclosure period in ppbv, Δt is the

enclosure period expressed in minutes, M the molar mass of N_2O–N ($28g$ mol^{-1}), P and T the atmospheric pressure (Pa) and temperature (K) (the measured temperature and pressure values were taken at 10am from the nearby weather stations located within 1 km of each site), R the ideal gas constant (8.314 J K^{-1} mol^{-1}), V the headspace volume of the closed chamber (m^3) and A the area covered by the base of the gas chamber (ha). This flux per base area was extrapolated to flux on a ha^{-1} d^{-1} basis. The annual cumulative N_2O emissions (over 365 days) were determined by integrating the calculated daily N_2O fluxes from Eq (1) using the trapezoidal integration method (de Klein and Harvey, 2012). The Emission Factor (EF%) was calculated for each treatment using equation 2 below

$$\text{EF\%} = [\text{Cum Flux } N_2\text{O-N }(_{treatment}) - \text{Cum Flux } N_2\text{O-N }(_{control})]/\text{N applied} *100 \qquad (2)$$

where:

EF% = Emission Factor (N_2O-N emitted as a % of fertiliser N applied)

Cum Flux N_2O–N ($_{treatment}$) = Cumulative N_2O-N emissions in g N_2O-N ha^{-1} yr^{-1} for the fertiliser treatment

Cum Flux N_2O–N ($_{control}$) = Cumulative N_2O-N emissions in g N_2O-N ha^{-1} yr^{-1} for the control treatment

N applied = Annual N application rate in kg ha^{-1} yr^{-1}

2.3 Soil and climatic parameters

Climatic measurements included daily air temperature (°C), atmospheric pressure (mbar), rainfall (mm), and soil temperature in the top 10 cm (°C). These were obtained from nearby weather stations (within 1 km of field sites) from the Met Éireann automatic weather stations at JC and MP and the Environmental Change Network weather station at HB.

Soils were sampled to a depth of 10 cm weekly for mineral N during the growing season and fortnightly in winter. These soil samples were extracted for mineral N on the day of

collection using 2M KCl at a ratio of 2:1 (v:w) extractant to soil at HB and at a ratio of 5:1 (v:w) extractant to soil at JC and MP. The NH_4^+-N, NO_2^--N and NO_3^--N concentrations were determined using an Aquakem 600 discrete analyser for JC and MP samples, and using a SKALAR automated continuous flow wet chemistry analyser (San++ System, Breda, The Netherlands) at HB. The gravimetric water content of the soil samples was also measured on each soil sampling occasion. Separate volumetric soil moisture measurements were taken on each gas sampling occasion using a hand held ML2x Theta Probe (Delta-T Devices Ltd., HH2, UK) and hourly volumetric moisture was logged at all sites using a CR10X Data logger (Campbell Scientific) with a minimum of four CS-625 Water Content Reflectometer (WCR) probes. The stone free bulk density at each site was used to calculate WFPS from the volumetric moisture content. Volumetric soil moisture data was first calculated from the gravimetric measurements and this was supplemented with theta probe and WCR volumetric data to provide better temporal resolution.

2.4 Statistical analysis

Statistical analysis was conducted using SAS v 9.3 (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.). To identify potential outliers in the dataset, the SAS PROC MIXED with residual and influence diagnostics allowed the identification of highly influential observations relative to others in the dataset. These potential outliers were identified using the restricted likelihood distance and further assessed to identify genuine outliers. In this assessment of the temporal data, only three individual flux measurements were judged to be true outliers; these outliers were subsequently excluded from the analysis (the values were 429, 320 and -14 g N_2O g N ha^{-1} d^{-1}). SAS code was also used to test the linearity of N_2O accumulation within the chamber headspace. If the slope of the linear regression line fit to the multiple sampling points was significantly different to zero (i.e. $P<0.05$) this group were assigned to the "non

zero flux" group; This group was further tested for the significance of the quadratic term for describing the relationship between N_2O flux and time; if the quadratic term was not significant the relationship was assumed to be linear as per Chadwick et al. (2014). A generalised linear mixed modelling approach was used to test for a fertiliser N treatment effect on annual N_2O-N loss using the PROC GLIMMIX procedure of SAS 9.3. The two factors analysed were the effect of formulation and the effect of combined site and year (site-year) on cumulative N_2O emissions. Cumulative N_2O data were first checked for normality before analysis. As the data were not normally distributed cumulative N_2O emission values were log transformed prior to analysis and then back transformed subsequently. Differences between fertiliser treatments were determined using the F-protected least significant difference (LSD) test at the 95% confidence level.

3. Results

3.1 Drivers of N$_2$O emissions

Climatic conditions and soil chemical and physical characteristics are shown in Table 1. Total rainfall for the growing season (1 March to 30 Sept) and annually (365 days after the first fertiliser application) are presented for each of the six site-years in addition to the 30 year long term average rainfall (LTA) and the 30 year growing season average rainfall (GSA).

3.1.1 Rainfall

Annual experimental year rainfall (365 days after the first fertiliser application) at HB exceeded the LTA rainfall by 26% in 2013 and by 18% in 2014 (Table 1). At MP annual rainfall exceeded LTA by 11% in 2013 but was 2% below LTA in 2014. JC had lower annual rainfall than LTA by 4% in 2013 and 11% in 2014.

The growing season rainfall (1 March to 30 Sept) at HB 2013 exceeded the GSA for that period by 17% (Table 2), while there was no difference between the growing season rainfall and the GSA at HB 2014. In 2013 and 2014 both MP and JC had lower growing season rainfall than the GSA rainfall by 20% and 37%, respectively in 2013 and by <1% and 17% respectively in 2014.

3.1.2 Soil texture / drainage class

Soil texture and drainage characteristics for the six site-years are presented in Table 1. The HB site had the highest clay content, which is reflected in its classification as a clay loam and its drainage status being classed as imperfect. It also had the highest cation exchange capacity (CEC) (28.5 cmol(+) kg^{-1} and 25.4 cmol(+) kg^{-1} in 2013 and 2014, respectively) and the highest values for loss on ignition (LOI) (14.3% and 12.54% in 2013 and 2014, respectively). The MP sites had the highest sand content (58.8 and 57.8% in 2013 and 2014, respectively)

and were the best drained sites in the experiment. The HB soils had a lower stone free bulk density than the other sites in both years (0.86 in 2013 and 0.79 in 2014). The stone-free bulk density at JC in 2014 was the highest (1.27), despite having been recently reseeded. The soil pH at all sites was <6, which was lower than the optimum pH of 6.0 - 6.5 for grassland.

3.1.3 Water filled pore space (WFPS)

The site-years exhibiting the highest (HB) and lowest (MP) WFPS in the experiment both occurred in 2013 (Fig 1a, 2a, 3a). In 2013 at HB the annual average WFPS was 68% and growing season average WFPS was 61% while at MP the annual average WFPS and growing season average WFPS was 43% and 39%, respectively. At JC the annual average WFPS and growing season average WFPS was 51% and 41% respectively. There was greater consistency in WFPS across sites in 2014. At HB the annual average WFPS was 62% and growing season average WFPS was 58%, while at MP the annual average WFPS and growing season average was 68% and 66%, respectively. At JC, the annual average WFPS was 59% and growing season average WFPS was 58%.

3.1.4 Soil mineral N

Soil NO_3^--N and NH_4^+-N concentrations were observed to increase following each fertiliser application (Fig 1b, 2b and 3b). Across all six site-years, CAN contributed a very similar size and pattern of peaks to both NH_4^+ and NO_3^- pools following fertiliser application (Figures 1b, 2b and 3b) while the urea formulations contributed mainly to the soil NH_4^+ pool, with much smaller NO_3^- concentrations. For example, following the first application at HB in 2013 (Figure 1b) the largest increases in both the NH_4^+ pool and the NO_3^- pool were observed in the CAN treatment, with maximum NH_4^+ and NO_3^- concentrations of 61.7 and 68.8 mg kg^{-1} soil, respectively. By comparison, the urea treatments contributed to the NH_4^+ pool in the

order urea+DCD, urea, urea+NBPT, urea+DCD+NBPT with maximum concentrations ranging from 51.7 (urea+DCD) to 27.4 (urea+DCD+NBPT) mg N kg^{-1} soil. High mineral N concentrations were associated with periods of low WFPS. For example, at MP in 2013 high soil mineral N was associated with low WFPS at applications 3, 4 and 5 which also coincided with low N$_2$O fluxes. Similarly at JC in 2013, high soil mineral N was associated with low WFPS at application 4.

3.2 Temporal nitrous oxide fluxes following fertiliser application

Non-linear gas accumulation within the chamber headspace was <10% at all sites (Table 2). N$_2$O fluxes displayed both high temporal and between treatment variation. The temporal emissions profile typically occurred as distinct flux episodes immediately after fertiliser application, with the largest fluxes often coinciding with elevated WFPS levels (Fig. 1c, 2c, 3c). The highest N$_2$O fluxes over the whole experiment were observed at the HB site during 2013, with both the longest sustained emissions (after the first fertiliser application on 18 March, Fig 1c) and the highest daily N$_2$O flux which occurred after the fourth fertiliser application on 24 June. N$_2$O emissions at HB remained high for approximately 3 weeks after the first fertiliser application and were associated with a high soil WFPS (88%), high NO$_3$-N concentrations (23.9 mg N kg^{-1}) and cold soil temperatures (2.5 °C), which would have limited plant N uptake. The highest daily flux of 863 g N$_2$O-N ha^{-1} d^{-1} was associated with a WFPS of 64%, 15.6 mm of precipitation on the previous day, high soil NO3-N concentrations and a soil temperature of 15 °C. N$_2$O emissions were very low following the fifth fertiliser application on 19 August. This was associated with a WFPS of 52% and the absence of any significant rainfall for 19 days after N application. At MP in 2013 the highest emissions occurred early in the growing season however, the fluxes were substantially lower than those recorded at HB (Fig. 1c). Relatively little N$_2$O loss was associated with the third,

fourth and fifth fertiliser application and this coincided with a drop in WFPS (Fig 2a) from an annual average WFPS of 48%, to monthly averages of 26% in July and 34% in August. Similarly at the JC site in 2013, minimal emissions occurred after the July application (Fig 3c), when the corresponding monthly average WFPS was 27%, half of the annual average WFPS of 54% (Fig 3a).

At HB in 2014 the highest daily N_2O fluxes were associated with the first and fourth N applications (340 and 187g N_2O-N ha^{-1} d^{-1}, respectively) and were associated with a WFPS of 88% and 66%, respectively (Fig 1a). At the MP site in 2014 the emissions profile exhibited a high degree of variability following the fifth application, with high emissions associated with a single block (block 5) which had an average WFPS which was 21% higher than the other blocks during this period (1 July to 1 Oct 2014). At JC in 2014 high daily fluxes occurred following fertiliser application except in July which was associated with a low soil WFPS. Across all sites in 2013, 78% of emissions>30 g N_2O-N ha^{-1} d^{-1} occurred at 60%-80% WFPS, the remainder occurred above this range. In 2014, 80% of the emissions >30 g N_2O-N ha^{-1} d^{-1} occurred at 60%-80% WFPS with 7% below this range and 13% above this range.

3.3 Impact of N formulation on cumulative N_2O emissions

There was a significant site-year by treatment interaction on cumulative N_2O emissions ($P<0.001$). At all sites, over the entire experimental period, the highest daily fluxes were dominated by the CAN treatment (Figures 1c, 2c and 3c). Across the six site-years the same pattern of treatment response was observed: cumulative N_2O loss was highest for CAN, followed by urea + NBPT, followed by urea alone (Table 3). The urea with DCD treatments (urea+DCD and urea+NBPT+DCD) resulted in the lowest N_2O emissions. The CAN treatment resulted in significantly higher N_2O emissions than all of the urea-based treatments

apart from urea+NBPT at JC in both 2013 and 2014, where although emissions were lower than CAN the difference was not significant (Table 3).

The highest cumulative N_2O emissions occurred at the HB site in 2013 and resulted in a loss of 8.1 kg N_2O-N ha^{-1} yr^{-1}. Emissions from urea and urea+NBPT were significantly lower than CAN at HB in 2013 at 1.1 and 1.2 kg N_2O-N ha^{-1} yr^{-1}, respectively. Addition of DCD to urea+NBPT lowered cumulative emissions further, but this reduction was only significant at MP in 2013 and JC in 2014. Cumulative emissions from urea+NBPT+DCD were significantly lower than CAN in all site years. Urea+DCD resulted in significantly lower cumulative emissions than CAN at all sites and although it reduced N_2O emissions compared with urea this was only significant at HB in 2013 (Table 3). Cumulative N_2O emissions from treatments containing DCD were not significantly different to the controls receiving no fertiliser N. The CAN/urea and urea+MIP treatments were assessed in two site years: CAN/urea treatment had significantly lower emissions than CAN in both site years and while urea+MIP had consistently lower N_2O emissions than CAN the difference was only significant in one site year. Neither the CAN/urea nor the urea+MIP treatments generated significantly different N_2O emissions to urea in either site year. CAN was the most variable treatment, with an across site-year coefficient of variation (cv) of 61%, while urea+NBPT and urea were less variable, with cvs of 29% and 14%, respectively.

3.4 N_2O emission factors

Direct EFs for each fertiliser formulation for each year are shown in Table 4. The CAN N_2O emission factors were the highest and most variable ranging from 0.58 to 3.81% and were significantly higher than the IPCC default value of 1% in three out of the six site-years. In contrast, the EFs for urea and urea+NBPT formulations were consistently lower than CAN

and less variable (ranging from 0.10 – 0.69%) and substantially lower than the IPCC default value. The inclusion of DCD in the urea granules generated the lowest EFs. Indeed, in some cases the cumulative N_2O emissions from the treatments containing DCD were lower than the control plots and hence generated small negative EFs (Table 4). Emission factors associated with the CAN/Urea treatment (two site-years) ranged from 0.22% to 0.24% while EF's for urea+MIP were between 0.1% and 0.59%.

4. Discussion

The main drivers of N_2O emissions in this experiment have been identified as: N formulation, climatic conditions, soil texture and drainage class.

4.1 The effect of N formulation on N_2O emissions

There was a clear association between fertiliser formulation and N_2O emissions. At all sites over the entire experimental period the highest daily N_2O fluxes were dominated by the CAN treatment, with elevated emissions occurring almost directly following a fertiliser application. At the HB site in particular, the highest emissions were produced in conditions ideal for denitrification of soil NO_3^--N. This was associated with higher than average growing season rainfall (+17%), combined with a high C content and a fine-textured gleysol which led to sustained high WFPS. In contrast the accumulation of NO_3^- and NH_4^+ in the soil at JC and MP in the same year coincided with periods where soil WFPS was low and hence N_2O emissions were low. Overall the current study showed that switching from CAN to any urea form significantly reduced direct N_2O emissions (with the exception of the urea+NBPT treatment in 2 out of 6 site years). A meta-analysis by Akiyama et al. (2010), showed that UIs were not effective in reducing N_2O from urea and they linked any reduction in N_2O emissions to increased plant assimilation of additional NH_4^+-N thereby reducing levels of nitrification to NO_3^- and potential denitrification losses. Some studies have shown that NBPT significantly reduced N_2O emissions relative to urea (Tian et al., 2015; Abalos et al., 2012), while in the present study urea+NBPT generated numerically higher emissions in five site years, being significantly higher in one site year only. This may be related to differences in management practices and environmental conditions between the studies which ranged from temperate (current study) to subtropical to Mediterranean climates. In the current study the nitrification inhibitor DCD was incorporated into the urea granule at manufacture which provided a very

targeted delivery compared with spraying a liquid solution of DCD onto the whole paddock (Di and Cameron, 2002; 2003; 2005). Comparisons of granular versus liquid DCD application at the same time and rate found no effect of formulation on N leaching or yield (Menneer et al., 2008). In New Zealand the general recommendation for DCD is 10 kg DCD ha^{-1} application^{-1} (Clough et al., 2011) while the effective application rate of DCD in the current study was only 1.39 kg DCD ha^{-1} application^{-1}, which represents 7 kg over the whole year compared to 20 kg in New Zealand (2x10 kg applications). Even at this low rate it reduced the N_2O emissions from urea to levels not significantly different to background. In New Zealand residue issues associated with the use of DCD in pastures were observed (Welten et al., 2016). Without a clear defined threshold concentration for DCD in food products, this is a potential issue for food safety. The more frequent application of DCD with fertilisation helped to overcome the degradation of DCD in soil (Cahalan et al. 2015). While both DCD and NBPT-stabilised urea mitigated N_2O emissions it will be important in the future to assess the impact of these inhibitor/stabiliser products on other soil nitrogen transformation processes such as mineralisation and immobilisation turnover (MIT) as this could provide insight into long term effects of these products on soil fertility. The addition of MIP to urea did not significantly reduce N_2O emissions compared with urea which is in agreement with Parkin and Hartfield (2014) who observed no reductions in cumulative N_2O emissions with MIP in corn (*Zea mays* L.). They proposed that this was due to significantly higher soil NO_3^-–N levels in the MIP treatment which drove higher cumulative N_2O emissions compared to other enhanced efficiency fertilisers. The same effect was observed in the current study.

The addition of N stabilisers to urea will have an impact on fertiliser cost. In New Zealand Monaghan et al., (2009) concluded that only the payment of a Carbon credit for reduced N_2O emissions would make the application of DCD in granular form (at a rate of 10 kg DCD ha^{-1})

economically viable. In contrast the urea+NBPT product is commercially available in the EU and while more expensive than straight urea, prices are lower than CAN on a per unit N basis offering the potential for farmers to save on fertiliser costs by switching formulation.

The current national emission limits for both GHGs and NH_3 are also set for further reduction; under forthcoming proposals, new GHG targets across Europe will seek to reduce emissions by at least 40% compared with 1990 levels by 2030 (Annex to the communication from the commission to the European Parliament and the Council (EU) (2015/81)), while changes proposed to the National Emissions Ceilings Directive will also require revised reduction targets for NH_3 emissions for Ireland of 5% below 2005 levels by 2030 (Annexes to the proposal for a Directive (EU) 2013/920). Switching fertiliser use from CAN to urea based products will mitigate direct N_2O emissions but may exacerbate NH_3 emissions, unless a urease inhibitor is used.

4.2 The effect of climatic conditions and soil type on N_2O emissions

One of the key parameters governing the N_2O emissions is soil moisture and its importance can be seen in the contrast between wetter and drier site-years at the same location. The highest cumulative emissions recorded in this experiment, in excess of 8 kg N_2O-N ha^{-1} yr^{-1} occurred in 2013 at HB where rainfall for the growing season was 17% higher than the GSA. In contrast in 2014 the emissions were lower (3.5 kg N_2O-N ha^{-1} yr^{-1}) when the growing season rainfall was in line with the GSA. A previous experiment conducted at HB in 2011 recorded total annual cumulative emissions for CAN of only 0.59 kg N_2O-N ha^{-1} yr^{-1} and this coincided with dry conditions at the time of fertiliser application and a growing season rainfall 7% below the GSA (McGeough unpublished). Other studies have found that controlling the extent of NO_3^- accumulation in soil influences the magnitude of N_2O emissions (McTaggart et al., 1997; Clayton et al., 1997). This is especially important in high

rainfall areas. The results of the current study show that replacing CAN with any urea form, especially in wet grassland, greatly reduced direct N_2O emissions. This is in agreement with Velthof et al. (1997); Clayton et al. (1997); Dobbie and Smith (2003); Jones et al (2007) and Smith et al. (2012).

Soil moisture is also influenced by soil texture and drainage class. At similar levels of precipitation soils with higher clay content will have higher field capacity and volumetric soil moisture content (Cornell University, 2015) compared to soils with low clay content and will be prone to anaerobic conditions after heavy rainfall. This will result in more frequent stimulation of either partial or total denitrification (depending on the soil redox potential) resulting in higher N_2O emissions from fine textured soils (Butterbach-Bahl and Gundersen, 2011). The HB soil texture was classified as a clay loam (gleysol) and was imperfectly drained with evidence of gleying (at 0.3m depth). In addition, drainage impeded soils tend to be low in oxygen and tend to lose a greater percentage of N as N_2O (Dennis et al., 2012) compared to well drained soils, with emissions from managed and grazed grasslands on peat soils among the highest emissions in the world (van Beek et al., 2011). Results from the current study demonstrated that emissions from CAN at HB were significantly higher than the other two sites, probably due to the higher denitrification potential of these soils combined with higher precipitation at this location especially in 2013. Different soil types have different N_2O sources under different soil moisture conditions due to inherent differences in hydro-conductivity. For example at a constant WFPS of 60% Pihlatie et al., (2004) showed that nitrification generated 70% of the total N_2O production in a sandy soil, while the majority of the total N_2O production originated from denitrification in a peat soil This is related to faster drainage following rainfall being associated with larger pores in the well-drained soil resulting in faster oxygen diffusion which, in turn, will reduce N_2O production via denitrification due to differences in available water content (van der Weerden

et al., 2010). There is also evidence that saturated soil conditions increased denitrifier populations in turf grass and both ammonia oxidiser and denitrifier communities under incubation (Mancino and Torello 1986, Di et al., 2014). Prolonged saturation of the soil at HB in 2013 may, over time, promote microbial community changes which could also contribute to the high N_2O emissions at this site. Long-term undisturbed grasslands will have a greater proportion of fungi to bacteria that could result in higher N_2O losses due to the fact that fungi lack the N_2O reductase enzyme to reduce N_2O to N_2 (Shoun et al., 1992, Laughlin et al., 2003). In addition soils with high clay content are more prone to soil compaction which further induces anoxic conditions favourable for denitrification by affecting oxygen availability and generating larger and longer lasting emissions (Bessou et al., 2010).

4.3 N_2O emission factors

The current study found that the emission factor for CAN ranged from 0.58 to 3.81%, and for urea formulations it ranged from 0.10% to 0.49%. The variation in CAN EF was highly site-year dependent while variation in urea EF was dependent on formulation (ie. whether NBPT or DCD was incorporated into the granule). Other studies have also found N_2O emissions were greater from NO_3^--based fertilisers than from urea (Dobbie and Smith 2003, Stehfest and Bouwman 2006, Kuikman et al., 2006 and Jones et al., 2007). The range of direct annual EFs in this experiment (0.02–3.81%) are similar to the ranges of EFs calculated by Dobbie and Smith (2003) in Scottish grasslands (1 to 3*%),* Kuikman et al., (2006) in the Netherlands (0.43 to 3%) and Jones et al., (2007) also in Scottish grassland (0.1-1.4%). In addition, Stehfest and Bouwman (2006) summarised 1125 published N_2O emissions measurements (not annual EFs) from agricultural fields and the range of emissions was from 0.79 to 5.64 kg N_2O-N ha^{-1}. Previous studies on N_2O losses in Irish grasslands (not annual EFs, annual EF's are calculated by subtracting the control) have shown a range in emissions from 0.7 to 4.9%

(Hyde et al., 2006, Rafique et al., 2011). In the current study urea reduced direct N_2O emissions compared to CAN at all sites, while urea+NBPT generated significantly higher emissions than urea in 2/6 site years. While the CAN/urea treatment also showed promising results, with similar N_2O emissions to NBPT-stabilised urea, it was only assessed in two site years and so further measurement is required. In order to conduct a thorough assessment of fertiliser form on total N_2O emissions, indirect N_2O emissions associated with NH_3 volatilisation and re-deposition need to be taken into account as volatilisation from urea has been observed to be substantially higher than that of CAN (Dobbie and Smith 2003; Watson et al., 1990). Nitrate leaching was not included in the indirect emissions estimate as no difference in leaching rates was expected between the fertiliser formulations (Singh et al., 1991). Combining the direct and indirect EFs (using the national emission factors of 13.7% for urea and 1.4% for CAN (Misselbrook et al., 2004; EMEP/EEA) for each fertiliser formulation (Table 5), shows N_2O emissions that would result from including re-deposition of N following NH_3 volatilisation. Despite the inclusion of indirect emissions, the total N_2O emissions from CAN were still higher than for any of the urea formulations.

The average direct EF for mineral fertiliser for all treatments across all sites in this study was 0.49%, considerably below the IPCC default of 1%. However, this single summary EF does not accurately reflect the treatment and site differences. Overall EFs, disaggregated by formulations and drainage class are presented in Table 6. Finally, if fertiliser formulation in Ireland was switched from CAN to urea+NBPT, it is possible to estimate the impact that this would have on the national inventory based on the results of this study. The potential reduction in direct N_2O-N emissions by switching formulation from CAN to urea+NBPT calculated using the average fertiliser form EFs (Table 6) is a saving of 1831 tonnes of N_2O-N per annum based on a CAN usage in Ireland of 168,000 tonnes of N (IFADATA, 2013).

While the size of EFs are driven by N formulation, climatic conditions, soil texture and drainage class, the results of this study indicate that by switching formulation from CAN to stabilised urea, N_2O emissions can be reduced by 73%. These estimates could be further improved by using a more detailed analysis of fertiliser usage by soil type.

There were difficulties in estimating the quantity of indirect emissions arising from re-deposition of NH_3 but these indirect emissions must be accounted for in order to generate robust EFs. In order to incorporate indirect emissions, the IPCC default value of 1% was used although, as shown in this study the direct N_2O EF from an ammonium source (urea or urea+NBPT) was much lower. If the default EF for urea 0.25% was used instead of the 1% default value, it would further lower the indirect emissions from urea based formulations.

5. Conclusion

Fertiliser N formulation, soil texture, drainage class and climatic conditions have been shown to have a significant effect on N_2O emissions. The highest daily fluxes were following fertiliser applications of CAN. Switching from CAN to any urea formulation significantly reduced direct N_2O emissions. It is likely that inherent differences in climate and soil properties at HB were responsible for the higher emissions from CAN. In conditions where urea fertiliser is susceptible to N loss through the volatilisation of NH_3, the addition of NBPT to urea would be effective at reducing losses from volatilisation. The emissions from urea+DCD and the double stabilised treatment were the lowest in this study, with N_2O emissions not significantly different to background levels. However, the addition of stabilisers to urea will have an impact on fertiliser costs. Inclusion of DCD in the urea granule may only be economic if a C credit is given for reduced N_2O emissions. In contrast the urea+NBPT product is commercially available in the EU and while it is more expensive than straight urea on a weight basis, it is cheaper than CAN on a per unit N basis, offering the

potential for farmers to save on fertiliser costs. Switching fertiliser use from CAN to any urea formulation controls the size of the NO_3^- pool in the soil and reduces the magnitude and the variability of the N_2O emissions, particularly in wet heavy soils that have a high denitrification potential. This strategy could reduce N_2O emissions by as much as 70%.

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References

2015/81 Annex to the communication from the commission to the European Parliament and the Council. The Paris Protocol - A blueprint for tackling global climate change beyond 2020.

2013/920 Annexes to the proposal for a Directive (EC) 1984/2003 of 18 December 2013 on the reduction of national emissions of certain atmospheric pollutants and amending Directive 2003/35/EC.

Abalos, D., Sanz-Cobena, A., Misselbrook, T. and 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. DOI:10.1016/j.chemosphere.2012.04.043

Akiyama, H., Xiaoyuan, Y. and Kazuyuki, Y. 2010. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis. *Global Change Biology*. 16:6, 1837–1846. DOI:10.1111/j.1365-2486.2009.02031.x.

Bessou, C., Mary, B., Léonard, J., Roussel, M., Gréhan, E. and Gabrielle, B. 2010. Modelling soil compaction impacts on nitrous oxide emissions in arable fields. *European Journal of Soil Science*. 61, 348-363. DOI:10.1111/j.1365-2389.2010.01243.x.

Bouwman, A.F., Boumans, L.J.M. and Batjes, N.H., 2002. Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochemical Cycles*. 16:4, 1-13. DOI: 10.1029/2001GB001811.

Butterbach-Bahl, K., Baggs, E.M., Dannenmann, M., Kiese, R. and Zechmeister-Boltenstern S. 2013. Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences*. 368:1621, 1-13. DOI: 10.1098/rstb.2013.0122.

Butterbach-Bahl, K and Gundersen, P. 2011. Nitrogen processes in terrestrial ecosystems in The European Nitrogen Assessment, eds. Mark A. Sutton, Cl Howard, Jan Willem Erisman, Gilles Billen, Albert Bleeker, Peringe Grennfelt, Hans van Grinsven and Bruna Grizzetti. Cambridge University Press, Cambridge, UK. Available at: http://hdl.handle.net/1854/LU-2042092. Accessed 1/12/15.

Cahalan, E., Minet, E., Ernfors, M., Müller, C., Devaney, D., Forrestal, P.J. and Richards, K.G. 2015. The effect of precipitation and application rate on DCD persistence and efficiency in two Irish grassland soils, *Soil Use and Management.* 31, 367–374. DOI: 10.1111/sum.12194.

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. and Dhanoa, M.S. 2014. Optimizing chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments. *European Journal of Soil Science.* 65:2, 295-307. DOI: 10.1111/ejss.12117.

Chambers, B. And Dampney, P. 2009. Nitrogen efficiency and ammonia emissions from urea-based and ammonium nitrate fertilisers. *International Fertiliser Society Proceedings.* 657: 1-20. ISSN1466-1314

Clayton, H., McTaggart, I.P., Parker, J., Swan, L. and Smith, K.A. 1997. Nitrous oxide emissions from fertilised grassland: A 2-year study of the effects of N fertiliser form and environmental conditions. *Biology and Fertility of Soils.* 263:1, 101-111. DOI: 10.1007/s003740050311.

Clough, T.J., Kelliher, F.M., Clark, H. and van der Weerden, T.J. 2011. Incorporation of the Nitrification Inhibitor DCD into New Zealand's 2009 National Inventory. Ministry of Agriculture and Forestry, 2011. Available at: https://www.mpi.govt.nz/document-vault/2949 Accessed on 8 April 2016.

Cornell University. 2015. Certified Crop Adviser (CCA) Program - Soil hydrology AEM. Available at: http://nrcca.cals.cornell.edu/soil/CA2/CA0212.1-3.php. Accessed 5/11/2015.

CSO 2012.Statistical Yearbook of Ireland 2012. Central Statistics Office, Cork. Available at: http://www.cso.ie/en/media/csoie/releasespublications/documents/statisticalyearbook/2012/c10agriculture.pdf. Accessed 28/9/2015.

Dampney, P.M.R., Richards, I. and Bhogal, A. 2003. Nitrogen fertilising materials - Report for Defra Project NT2601 Available at http://randd.defra.gov.uk/Document.aspx?Document=NT2601_4055_FRP.doc. Accessed 21/11/15.

Davidson, E.A. and Swank, W.T. 1986. Environmental parameters regulating gaseous nitrogen losses from two forested ecosystems via nitrification and denitrification. *Applied and Environmental Microbiology.* 52, 1287–1292. DOI: 0099-2240/86/121287-06$02.00/0.

Davidson, E. A., Keller, M., Erickson, H. E., Verchot, L.V. and Veldkamp, E. 2000. Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides: Using two functions based on soil nitrogen availability and soil water content, the hole-in-the-pipe model characterizes a large fraction of the observed variation of nitric oxide and nitrous oxide emissions from soils. *BioScience*. 50, 667-680. DOI: 10.1641/0006-3568(2000)050[0667:TACMOS]2.0.CO;2

Davidson, E.A. 2009. The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860. *Nature Geoscience.* 2:9, 659–662. DOI: doi:10.1038/ngeo608.

de Klein, C.A.M. and 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: 28/9/015.

Dennis, S.J., Cameron, K. C., Di, H. J., Moir, J. L., Staples, V., Sills, P. and Richards, K.G. 2012. Reducing nitrate losses from simulated grazing on grassland lysimeters in Ireland using a nitrification inhibitor (Dicyandimide). *Biology and Environment*: *Proceedings of the Royal Irish Academy.* 112B:1, 79-89. DOI: 10.3318/BIOE.2011.24.

Di, H.J. and Cameron, K.C. 2002. The use of a nitrification inhibitor, dicyandiamide (DCD), to decrease nitrate leaching and nitrous oxide emissions in a simulated grazed and irrigated grassland. *Soil Use and Management*. 18 395–403. DOI: 10.1111/j.1475-2743.2002.tb00258.x.

Di, H.J. and Cameron K.C. 2003. Mitigation of nitrous oxide emissions in spray—irrigated grassland by treating the soil with dicyandiamide, a nitrification inhibitor. *Soil Use and Management*. 19, 284–290. DOI: 10.1111/j.1475-2743.2003.tb00317.x

Di, H.J. and Cameron K.C. 2005. Nitrous oxide emissions from two dairy pasture soils as affected by different rates of a fine particle suspension nitrification inhibitor, dicyandiamide. *Biology and Fertility of Soils*. 42:6 472-480. DOI: 10.1007/s00374-005-0038-5.

Di, H.J., Cameron, K.C., Podolyan, A. and Robinson, A. 2014. Effect of soil moisture status and a nitrification inhibitor, dicyandiamide, on ammonia oxidizer and denitrifier growth and nitrous oxide emissions in a grassland soil. *Soil Biology and Biochemistry.*73, 59–68. DOI: doi:10.1016/j.soilbio.2014.02.011.

Dobbie, K.E. and Smith, K.A. 2003. Impact of different forms of N fertilizer on N_2O emissions from intensive grassland. *Nutrient Cycling in Agroecosystems.,* 67,37–46. DOI: 10.1023/A:1025119512447.

Duffy, P., Hanley, E., Hyde, B., O'Brien, P., Ponzi, J., Cotter, E., and Black, K. 2014. Ireland National Inventory Report 2014, Greenhouse Gas Emissions 1990–2012. Reported to the United Nations Framework Convention on Climate Change. Environmental Protection Agency, Johnstown Castle Estate, Co. Wexford, Ireland.

Ellison, S.L.R., Barwick V.J. and Duguid Farrant, T.J. 2009. Practical Statistics for the Analytical Scientist A Bench Guide 2nd Edition. The Royal Society of Chemistry, Cambridge, UK.

EMEP/EEA. 2013. Air Pollutant Emission Inventory Guidebook. EEA technical Report No. 10. 2013.

Engel, R.E., Towey, B.D. and Gravens, E., 2015. Degradation of the Urease Inhibitor NBPT as Affected by Soil pH. *Soil Science Society of America Journal.* 79(6), pp.1674-1683. DOI:10.2136/sssaj2015.05.0169.

FAOSTAT. 2015. Food and Agriculture Organisation of the United Nations Statistics Division, Domains, Fertilisers, archive available at http://faostat3.fao.org/download/R/RA/E. Accessed 15/9/15.

Forrestal, P.J., Harty, M.A., Carolan, R., Lanigan, G.J., Watson, C.J., Laughlin, R.J., McNeill, G., Chambers, B.J. and Richards, K.G. 2015. Ammonia emissions from urea, stabilised urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland. *Soil use and Management*. Published online: Nov 2015. DOI: 10.1111/sum.12232/

Fox, R. H.; Bandel, V. A. 1986. Nitrogen utilization with no-tillage. In: No tillage and surface-tillage Agriculture. The tillage revolution [Sprague, M.A. and Triplett, G.B. (eds)] John Wiley, New York, 117-148.

Gardiner, M.J. and Radford, T. 1980. Soil Associations of Ireland and Their Land Use Potential. Explanatory Bulletin to Soil Map of Ireland 1980. National Soil Survey of Ireland An Foras Talúntais (The Agricultural Institute) Dublin, Ireland.

Hyde, B.P., Hawkins, M.J., Fanning, A.F., Noonan, D., Ryan, M., O'Toole, P. and Carton, O.T. 2006. Nitrous oxide emissions from a fertilized and grazed grassland in the South East of Ireland. *Nutrient Cycling in Agroecosystems.* 75, 187-200. DOI: 10.1007/s10705-006-9026-x.

IFADATA 2013. International Fertiliser Industry Association: available at http://ifadata.fertilizer.org/ucSearch.aspx. Accessed 15/9/15.

IPCC - Intergovernmental Panel on Climate Change - 2007 Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J. Lean, J., Lowe, D.C. Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M. and Van Dorland, R. 2007: Changes in Atmospheric Constituents and in Radiative Forcing. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., Qin, D. Manning, M. Chen, Z. Marquis, M. Averyt, K.B. Tignor M. and Miller, H.L. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC - Intergovernmental Panel on Climate Change – 2014. Smith, P., Bustamante, M. Ahammad, H. Clark, H., Dong, H., Elsiddig, E. A., Haberl, H., Harper, R., House, J., Jafari, M., Masera, O., Mbow, C. Ravindranath, N. H., Rice, C. W., Robledo Abad, C., Romanovskaya, A., Sperling, F. and Tubiello, F. 2014: Agriculture, Forestry and

Other Land Use (AFOLU). In: Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickemeier, P., Kriemann, B., Savolainen, J., Schlömer, S., von Stechow, C., Zwickel, T. and Minx, J.C. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jones, S.K., Rees, R.M., Skiba, U.M. and Ball, B.C. 2007. Influence of organic and mineral N fertiliser on N_2O fluxes from a temperate grassland. *Agriculture, Ecosystems & Environment.* 121: 1–2, 74–83. DOI: 10.1016/j.agee.2006.12.006

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. and Saggar, 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.

Kelliher, F.M., Cox, N., van der Weerden, T.J., de Klein, C.A.M., Luo, J., Cameron, K.C., Di, H.J., Giltrap, D. and Rys, G. 2014. Statistical analysis of nitrous oxide emission factors from pastoral agriculture field trials conducted in New Zealand. *Environmental Pollution.* 186, 63-66. DOI: 10.1016/j.envpol.2013.11.025.

Kuikman, P.J., van der Hoek, K.W., Smit, A., Zwart, K., 2006. Update of emission factors for nitrous oxide from agricultural soils on the basis of measurements in the Netherlands. Alterra report 1217. Pp. 40. ISSN 1566-7197

Lata, J. C., Degrange, V., Raynaud, X., Maron, P. A., Lensi, R., and Abbadie, L. 2004. Grass populations control nitrification in savanna soils. *Functional. Ecology.* 18, 605–611. DOI: 10.1111/j.0269-8463.2004.00880.x

Laughlin, R.J., Rütting, T., Müller, C., Watson, C.J. and Stevens, R.J. 2003. Effect of acetate on soil respiration, N_2O emissions and gross N transformations related to fungi and bacteria in a grassland soil. *Applied Soil Ecology.* 42:1, 25–30. DOI: 10.1016/j.apsoil.2009.01.004.

Mancino, C.F. and Torello, W.A. 1986. Enumeration of denitrifying microbial populations in turf. *Plant and Soil.* 96:1, 149-151. DOI: 10.1007/BF02375006.

McTaggart, I.P., Clayton, H., Parker, J., Swan, L. and Smith, K.A. 1997. Nitrous oxide emissions from grassland and spring barley, following N fertiliser application with and without nitrification inhibitors. *Biology and Fertility of Soils*. 25:3, 261-268. DOI: 10.1007/s003740050312.

Meixner, F. and Yang, W. 2006. Biogenic Emissions of Nitric Oxide and Nitrous Oxide From Arid AND Semi-Arid Land. In: D'Odorico, P. & Porporato, A. (eds.) *Dryland Ecohydrology*, 233–255.

Menneer, J.C., Sprosen, M.S. and Ledgard, S. F. 2008. Effect of timing and formulation of dicyandiamide (DCD) application on nitrate leaching and pasture production in a Bay of Plenty pastoral soil. *New Zealand Journal of Agricultural Research*. 51:3, 377-385. DOI: 10.1080/00288230809510468.

Misselbrook, T.H., Sutton, M.A. and Scholefield, D. 2004. A simple process-based model for estimating ammonia emissions from agricultural land after fertilizer applications. *Soil Use and Management.* 20, 365-372. DOI: 10.1111/j.1475-2743.2004.tb00385.x.

Monaghan R.M., Smith L.C. and Ledgard S.F. 2009. The effectiveness of a granular formulation of dicyandiamide (DCD) in limiting nitrate leaching from a grazed dairy pasture. *New Zealand Journal of Agricultural Research.* 52,145–159. DOI: 10.1080/00288230909510499.

Parkin, T.B. and Hatfield, J.L. 2014. Enhanced Efficiency Fertilizers: Effect on Nitrous Oxide Emissions in Iowa. *Agronomy Journal.* 106:2, 694-702. DOI: 10.2134/agronj2013.0219.

Pihlatie, M., Syvasalo, E., Simojoki, A., Esala, M. and Regina, K. 2004. Contribution of nitrification and denitrification to N_2O production in peat, clay and loamy sand soils under different soil moisture conditions. *Nutrient Cycling in Agroecosystem.* 70,135-141. DOI: 10.1023/b:fres.0000048475.81211.3c.

Rafique, R., Hennessy, D. and Kiely, G. 2011. Nitrous Oxide Emission from Grazed Grassland Under Different Management Systems. *Ecosystems.* 14:4, 563-582. DOI: 10.1007/s10021-011-9434-x.

Reeves, S. and Wang, W., 2015. Optimum sampling time and frequency for measuring N 2 O emissions from a rain-fed cereal cropping system. *Science of The Total Environment.* 530, 219-226. DOI: 10.1016/j.scitotenv.2015.05.117.

Saggar, S., Hedley, C.B., Giltrap, D.L., Lambie, S.M., 2007. Measured and modelled estimates of nitrous oxide emission and methane consumption from a sheepgrazed pasture. *Agriculture, Ecosystems & Environment.* 122, 357–365. DOI: 10.1016/j.agee.2007.02.006.

Schaufler, G., Kitzler, B., Schindlbacher, A., Skiba, U., Sutton, M. A. and Zechmeister-Boltenstern, S. 2010. Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature. *European Journal of Soil Science.* 61, 683-696. DOI: 10.1111/j.1365-2389.2010.01277.x.

Shelton, D.R.; Sadeghi, A.M. and McCarty, G.W. 2000: Effect of soil water content on denitrification during crop cover. *Soil Science.* 165, 365-371. DOI: 10.1097/00010694-200004000-00007.

Shoun, H., Kim, D.H., Uchiyama, H. andSugiyama, J. 1992. Denitrification by fungi. *FEMS Microbiology Letters*. 94, 277‑281. DOI: 10.1111/j.1574-6968.1992.tb05331.x.

Singh B., Singh Y., Khind C.S. and Meelu O.P. 1991. Leaching losses of urea-N applied to permeable soils under lowland rice. *Fertilizer Research.* 28: 179–184. DOI: 10.1007/BF01049748.

Smil, V. 2001. Feeding the World: A Challenge for the Twenty-First Century. Massachussets Institute of Technology, USA.

Smith, K. A. and Dobbie, K. E. 2001.The impact of sampling frequency and sampling times on chamber-based measurements of N_2O emissions from fertilized soils. *Global Change Biology*. 7:8, 933- 945. DOI: 10.1046/j.1354-1013.2001.00450.x,

Smith, L.C.; de Klein, C.A.M.; Monaghan R.M.; Catto W.D. 2008. The effectiveness of DCD in reducing nitrous oxide emissions from a cattle grazed winter forage crop in Southland, New Zealand. *Australian Journal of Experimental Agriculture*. 48, 160-164. DOI: 10.1071/EA07262.

Smith, K.A., Dobbie, K.E., Thorman, R., Watson, C.J., Chadwick, D.R., Yamulki, S. Ball,B.C., 2012. The effect of N fertilizer forms on nitrous oxide emissions from UK arable land and grassland. *Nutrient Cycling in Agroecosystems*. 93, 127-149. DOI: 10.1007/s10705-012-9505-1.

Soussana, J.F., Allard, V. Pilegaard, K. Ambus, P., Amman, C. Campbell, C. Ceschia, E., Clifton-Browe, J. Czobel, S. Domingues, R., Flechard, C. Fuhrer, J. Hensen, A. Horvaith, L. Jones, M. Kasper, G. Martin, C. Nagy, Z. Neftel, A. Raschi, A. Baronti, S., Rees, R.M. Skiba., U., Stefani, P. Manca, Sutton, G., Tuba, M. Z. and Valentini, R. 2007. Full accounting of the greenhouse gas (CO_2, N_2O, CH4) budget of nine European grassland sites. *Agriculture, Ecosystems and Environment*. 121, 121–134. Available at: http://hdl.handle.net/2160/11727. Accessed 1/12/15.

Stehfest, E. and Bouwman, L .2006. N_2O and NO emission from agricultural fields and soils under natural vegetation. *Nutrient Cycling in Agroecosystems.* 74:3, 207-228. DOI: 10.1007/s10705-006-9000-7

Subbarao, G. V., Ishikawa, T., Ito, O., Nakahara, K., Wang, H. Y. and Berry, W. L. (2006). A bioluminescence assay to detect nitrification inhibitors released from plant roots: a case study with Brachiaria Humidicola. *Plant and Soil*. 288.1-2: 101-112. DOI: 10.1007/s11104-006-9094-3.

Subbarao, G. V., Sahrawat, K. L., Nakahara, K., Ishikawa, T., Kishii, M., Rao, I. M., Hash, C. T., George, T. S., Srinivasa Rao, P., Nardi, P., Bonnett, D., Berry, W., Suenaga, K. and. Lata, J. C .2012. Biological Nitrification Inhibition—A Novel Strategy to Regulate Nitrification in Agricultural Systems. *Advances in Agronomy.* 114, 249-302. DOI: 10.1016/B978-0-12-394275-3.00001-8

Syakila ,A. and Kroeze C. 2011. The global nitrous oxide budget revisited. *Greenhouse Gas Measurement and Management*. 1:1, 17-26. DOI: 10.3763/ghgmm.2010.0007

Tian, Z., Wang, J.J., Liu, S., Zhang, Z., Dodla, S.K. and 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. *Science of The Total Environment*. 533, 329-338. DOI:10.1016/j.scitotenv.2015.06.147

Van Beek, C.L., Pleijter, M.M. and Kuikman, P.J. 2011. Nitrous oxide emissions from fertilized and unfertilized grasslands on peat soil. *Nutrient Cycling in Agroecosystems*. 89, 453-461. DOI: 10.1007/s10705-010-9408-y.

van der Weerden, T., de Klein, C. and Kelliher,F.2010. Influence of pore size distribution and soil water content on N_2O response curves. Proceedings of 2010 19th World Congress of Soil Science, Soil Solutions for a Changing World. August 2010, Brisbane, Australia.

van der Weerden, T. J., Kelliher, F. M. and de Klein C. A.M. 2012. Influence of pore size distribution and soil water content on nitrous oxide emissions. *Soil Research*, 50:2. 125-135. DOI: 10.1071/SR11112.

van der Weerden, T. J., Clough, T.J. and Styles, T.M., 2013, Using near-continuous measurements of N_2O emission from urine-affected soil to guide manual gas sampling regimes. *New Zealand Journal of Agricultural Research*. 56. 60-76. DOI: 00288233.2012.747548.

Velthof GL, Oenema O, Postma R and Van Beusichem ML. 1997. Effects of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland. *Nutrient Cycling in Agroecosystems*. 46, 257–267. DOI: 10.1007/BF00420561.

Venterea, R. T., Burger, M. and Spokas, K. A., 2005. Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *Journal of Environmental Quality*. 34, 1467-1477. DOI: 10.2134/jeq2005.0018.

Watson, C.J., Stevens R.J. and Laughlin R.J. 1990. Effectiveness of the urease inhibitor NBPT (N-(n-butyl) thiophosphoric triamide) for improving the efficiency of urea for ryegrass production. *Fertilizer Research*. 24: 11-15. DOI: 10.1007/BF01073142

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. 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 volatilization from surface-applied urea. *Soil Use and Management*. 24: 246–253. DOI: 10.1111/j.1475-2743.2008.00157.x

Watson, C.J., Laughlin, R.J & McGeough, K.L. 2009. Modification of nitrogen fertilisers using inhibitors: Opportunities and potentials for improving nitrogen use efficiency. Proceedings. The International Fertiliser Society. No 658, 1-40. ISSN1466-1314

Welten, B.G., Ledgard, S.F., Balvert, S.F., Kear, M.J. and Dexter, M.M., 2016. Effects of oral administration of dicyandiamide to lactating dairy cows on residues in milk and the efficacy of delivery via a supplementary feed source. *Agriculture, Ecosystems & Environment*. 217, 111-118. DOI:10.1016/j.agee.2015.10.013

Zaman, M., Nguyen, M. L., Blennrhassett, J. D. & Quin, B. F. 2008. Reducing NH_3, N_2O and NO3--N losses from a pasture soil with urease or nitrification inhibitors and elemental S-amended nitrogenous fertilisers. *Biology and Fertility of Soils*: 44, 693-705. DOI: 10.1007/s00374-007-0252-4.

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