Assessment of nitrous oxide emission factors for arable and grassland ecosystems

M. O’Neill, L. Gallego-Lorenzo, G. J. Lanigan, P. D. Forristal and B. A. Osborne

Abstract
We quantified seasonal nitrous oxide (N₂O) emissions and the associated emission factors (EFs) from: (i) winter oilseed rape (WOSR) cultivated under conventional tillage (CT) and strip tillage (ST) at four fertilizer rates (0, 160, 240 and 320 kg N ha⁻¹) in 2014/2015, and (ii) grassland plots receiving no fertilizer (0 kg N ha⁻¹), or mineral nitrogen (67 kg N ha⁻¹), and either cattle or pig slurry (50, 100 and 200 m⁻³ ha⁻¹). Greater fluxes were observed at higher soil temperatures and a higher water filled pore space, suggesting that denitrification was the main source of N₂O-N from the applied fertilizer/slurry. For WOSR, the N₂O EFs ranged from 0.03 to 1.20% with no effect of the cultivation practice on EFs for equal rates of nitrogen fertilizer. Lower EF values were linked to differences in plant growth at individual sites rather than a specific management effect. For the grassland, the N₂O EFs were highly variable, ranging from −0.70 to 0.49%, but were generally the highest in treatments receiving the highest concentrations of slurry. The EF values for WOSR illustrate that the Tier 1 approach for calculating EFs may be inadequate and the identification of site-specific effects can aid in refining N₂O EF inventories. For the grassland plots all the EFs were significantly lower than the IPCC default values. Although the reason(s) for the low EFs with slurry amendments on grassland is not known, ammonia volatilization could decrease the pool of inorganic N that is available to nitrifying bacteria thereby lowering N₂O fluxes.

Contact
M. O’Neill, macdara.onell@teagasc.ie, Teagasc, Environmental Research Centre, Wexford, Ireland

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1. Introduction

Agriculture contributes c. 50–70% of the global anthropogenic nitrous oxide (N\textsubscript{2}O) emissions (Smith 2017; Tian et al. 2019). Agricultural expansion and the increasing use of nitrogen (N) fertilizers are considered a large source of this N\textsubscript{2}O (Ciais et al. 2014). In the atmosphere, N\textsubscript{2}O is a potent greenhouse gas (GHG) and a strong ozone-depleting substance in the stratosphere (Ravishankara et al. 2009) with an atmospheric lifetime of \(\sim\)116 years (Prather et al. 2015). The current atmospheric N\textsubscript{2}O concentration is 330 ppb and is rising at a rate of 0.73 ppb year\(^{-1}\) (Ciais et al. 2014). Quantifying N\textsubscript{2}O emissions from agricultural activities is therefore an important process for understanding the source and magnitude of N\textsubscript{2}O production.

In Ireland, agriculture is responsible for 33.3% of the total GHG emissions (Duffy et al. 2019) with N\textsubscript{2}O accounting for 31% of these emissions. Nitrogen fertilization is responsible for 38% of this figure and is considered a large source of N\textsubscript{2}O loss from agricultural soils (Lanigan et al. 2018). The application of mineral and organic N fertilizer tends to increase the amount of ammonium (NH\textsubscript{4}\textsuperscript{+}) and nitrate (NO\textsubscript{3}\textsuperscript{−}) in the soil which can lead to greater emissions of N\textsubscript{2}O. The two main microbial processes that produce N\textsubscript{2}O are nitrification, the oxidation of NH\textsubscript{4}\textsuperscript{+} to nitrite (NO\textsubscript{2}\textsuperscript{−}) and NO\textsubscript{3}\textsuperscript{−}, and denitrification, the reduction of NO\textsubscript{3}\textsuperscript{−} to gaseous N\textsubscript{2}O and dinitrogen gas (N\textsubscript{2}) (Beauchamp 1997; Hu et al. 2015). Nitrous oxide fluxes are also influenced by soil moisture or water-filled pore space (WFPS), soil temperature, pH, labile carbon (C) availability, oxygen concentration and soil texture (Beauchamp 1997; Dobbie and Smith 2003; Ball 2013; Hu et al. 2015). Additionally, N\textsubscript{2}O displays high spatiotemporal variability (Butterbach-Bahl et al. 2013) making it difficult to constrain fluxes on regional scales.

The Intergovernmental Panel on Climate Change (IPCC) has refined its Tier 1 methodology for assigning emission factors (EF) to agricultural activities (IPCC 2019). In general, however, a default value of 1% is used to estimate direct N\textsubscript{2}O-N emissions from fertilizer application on managed agricultural soils (Duffy et al. 2019). There are, however, large uncertainties associated with these Tier 1 values, which might be reduced if the EFs could be further disaggregated, based on environmental and management-related factors. It is also generally assumed that N\textsubscript{2}O emissions increase linearly with N fertilizer rate, despite evidence for non-linear (Kim et al. 2013; Shcherbak et al. 2014) and exponential (McSwiney and Robertson 2005; Walter et al. 2015) relationships, which could complicate EF assessments.

In Ireland, tillage represents 8–9% (300,000 ha) of the total national agricultural area, with barley (spring/winter varieties) comprising 64% of the area devoted to arable crops (CSO 2019). Earlier research conducted on spring barley reported N\textsubscript{2}O EF values of 0.6% (Abdalla et al. 2010) and \(\leq\)0.49% (Roche et al. 2016), both considerably lower than the IPCC default value. There is, however, a scarcity of data published on other crop types and/or different management or cultivation practices.

Approximately 91% of Ireland’s agricultural area is, however, devoted to grassland production (CSO 2019) and this has been the focus of most of the research on N\textsubscript{2}O fluxes. Disaggregated N\textsubscript{2}O EFs have been reported for mineral fertilizer formulations, cattle excreta, and interactions between fertilizer and excreta, across contrasting soil types (Hyde et al. 2006; Harty et al. 2016; Krol et al. 2016; Maire et al. 2020). However, little attention, has been directed at the amount of N\textsubscript{2}O emitted from organic (slurry/manure)
applications to grassland. In one of the only documented studies, Bourdin et al. (2014) reported an EF value of 0.8% for cattle slurry applications, which also is lower than the IPCC default value of 1%.

Crop type, slurry treatment and cultivation practice may also influence N$_2$O EFs through their effect on N retention/fluxes but are rarely, if ever, accounted for, nor is N fertilizer management practice (timing, rate etc.) or soil type. It is therefore difficult to provide appropriate consolidated EFs and this may lead to significant under or over-estimates of regional N$_2$O emissions. The objective of this study was to quantify N$_2$O emissions and the associated EFs according to different agronomic practices at arable and grassland sites. In the arable study, winter oilseed rape (WOSR) was examined under both conventional tillage (CT) and strip tillage (ST) at varying N fertilizer rates. In the grassland study, the effect of N fertilizer type (mineral, organic) and application rate was assessed at a long-term site (>40 years). Importantly, there is very little information on how long-term management practices influence EFs and most studies have generally been conducted over much shorter time scales (<5 years). Our hypotheses were that: (i) strip tillage, through an increase in soil moisture, due to reduced soil disturbance, would increase N$_2$O emissions and associated EFs compared to CT systems, and (ii) N$_2$O EFs would vary according to fertilization treatment (mineral/slurry) and application rate in grasslands.

2. Materials and methods

2.1. Experimental sites

2.1.1. Arable experiment

This experiment was established on two long-term arable sites in south-east Ireland: the Sawmills field at Oakpark Research Centre, Co. Carlow (52°85′N, −6°94′W) in 2014 and the Kearns Field at Knockbeg, Co. Laois (52°86′N, −6°94′W) in 2015, which is located ~5 km from the Teagasc Crops Research Centre. The region has a 30-year mean annual rainfall of 823 mm and an average daily temperature of 9.3°C from 1982–2002.

The Oakpark site is classified as a well-drained eutric cambisol (c. 60% sand, 27% silt, 12% clay) mainly under spring barley production and over-winter green cover (mustard, natural regeneration) from 2006 onwards (Conry and Ryan 1967; Premrov 2011). It has a relatively shallow sandy and gravelly topsoil with a low soil moisture holding capacity (40%) (Conry and Ryan 1967; Premrov 2011; Abdalla et al. 2014). The Knockbeg site is classified as a well-drained haplic luvisol (44% sand, 34% silt, 22% clay; 0–30 cm) overlying a sandy clay loam (Conry and Ryan 1987; Fortune et al. 2006). It was originally a permanent pasture until conversion to tillage and continuous cropping in the mid-1990s (Van Groenigen et al. 2010).

The experiments at Oakpark and Knockbeg were laid out as a randomized block and randomized split-plot design, respectively, with four replications. The main plots were conventional (CT) and strip tillage (ST) with sub plots (25 m × 5 m) receiving four rates (0, 160, 240 and 320 kg N ha$^{-1}$) of calcium ammonium nitrate (CAN).

Winter oilseed rape (Brassica napus cv. Compass) was sown by CT and ST at a rate of 60 seeds m$^{-2}$ on the 27$^{th}$ August in 2013 (Oakpark) and on the 26/27 August 2014 (Knockbeg). Conventional tillage involved soil inversion to a depth of 250 mm followed by two passes with a ring roller. Seed was sown at 125 mm row spacing using a cultivator drill
Strip tillage is a non-inversion system operating at a similar working depth to ploughing (250 mm). In this setup, the seed is sown directly into cultivation strips leaving largely undisturbed soil in the inter-row spacing between the plants (HE-VA, Multi-seeder, UK). Management information for each site is described in Table S1.

### 2.1.2. Grassland experiment
The grassland experiment was established in 1970 on a pre-existent sward of perennial ryegrass (*Lolium perenne*), at the Agri-food and Biosciences Institute at Hillsborough (54° 27′N, 6°4′W), County Down, Northern Ireland, U.K. (Irish Grid Reference J 244,577). The site is considered to be comparable to a large proportion of the grassland area in Ireland and the north-western parts of the U.K. (Christie 1987). The soil is a dystric cambisol (42% sand, 24% silt and 34% clay) developed on glacial till overlying Silurian shales and greywackes with an organic matter content of 4.25% (Murphy et al. 2005). The elevation of the site is about 120 m above sea level. For the period 1970 to 2017 the mean annual precipitation was 894.2 mm and mean maximum and minimum temperatures were 12.3 and 5.7°C respectively (Fornara et al. 2016).

There were eight treatments with six replicates each giving a total of 48 plots (plot size: 29.7 m²) in a randomized-block design separated by herbicide sprayed lines. The treatments were: unfertilized control (Control), NPK fertilization (200 kg N, 32 kg P, 160 kg K ha⁻¹ yr⁻¹), cattle slurry and pig slurry applied at low (L: 50 m³ ha⁻¹), medium (M: 100 m³ ha⁻¹) and high (H: 200 m³ ha⁻¹) rates. The mean N content of the slurries over a 10 year period was 160, 320 and 640 kg N ha⁻¹ yr⁻¹ for cattle slurry, and 130, 270 and 540 kg N ha⁻¹ for pig slurry (Christie 1987; Fornara et al. 2016).

The fertilizer and slurry treatments were applied by hand and by watering can, respectively, in three equal dressings, first in spring and again immediately after the first and second cuts. The slurry application dates were the 15th March 22nd May and 21 July 2016. The sward was cut three times on the 21st May 20th July and 28 September 2016 with a Haldrup harvester. For convenience, the three growth periods are described as T1 (15th March to 21st May), T2 (21st May to 20th July) and T3 (21st July to 28th September).

Plant communities varied according to the fertilizer treatments (Fig. S1). Overall, perennial ryegrass, (*Lolium perenne*), meadow grass (*Poa sp.*) and creeping bent (*Agrostis sp.*) dominated many of the swards (32–83%). The fescues (*Festuca rubra* and *Festuca ovina*), velvet grass (*Holcus lanatus*), timothy grass (*Phleum pratense*), and white clover (*Trifolium repens*), comprised 71% and 66% of the plants species in the Control and Pig (L) treatments, respectively. The plant species composition in Fig. S1 represents the average values for the 1981, 2006 and 2016 seasons (Christie 1987; Liu et al. 2010; Fornara et al. 2016).

### 2.2. Nitrous oxide sampling and analysis
At the arable site, daily N₂O fluxes were measured using the static closed chamber technique (Chadwick et al. 2014) fitted over permanently installed collars. Chambers were only deployed for the actual measurements and removed afterwards. An air sample within the headspace was withdrawn through a stopcock fitted to the chamber vent using a 20-ml polypropylene syringe (BD Plastipak, Spain). The air inside the chamber was mixed by flushing slowly with the syringe plunger twice prior to the withdrawal of the gas.
sample. Using a fitted hypodermic needle, the sample was immediately transferred into a pre-evacuated 7 ml glass exetainer (Sigma-Aldrich, UK) fitted with double wadded septa or caps (Labco, High Wycombe, UK). The exetainers were injected with a 12-ml sample to create an overpressure and prevent back diffusion of ambient air.

Chambers were enclosed for forty minutes between 9.00 and 13.00 daily (Reeves and Wang 2015). After nitrogen fertilization, gas was sampled at a frequency of four times per week for two weeks, twice a week for two weeks and then once a week until harvest. Four ambient air samples were taken near ground level before and after each sampling occasion to obtain a surrogate time zero (T0) sample for each chamber (Chadwick et al. 2014). The linearity of N2O accumulation was determined on fifteen occasions using four time points extending to at least an hour (T0, T20, T40, T60) in the CT320 and ST320 plots. Gas accumulation inside the chamber could be described by linear and quadratic functions. Over 40 minutes, however, linear regression (r² = 0.997) was identified as the most suitable regression fit (80% linear, 13% quadratic, 6% no flux).

Analysis of N2O concentrations were carried out with a Bruker Gas Chromatograph with a 63Ni electron capture detector (ECD) at 300°C (Bruker, Germany). Samples were injected into the GC using a Combi-PAL auto-sampler (CTC Analytics AG, Switzerland). Results were expressed by volume (ppmv) and converted to mass units for daily (g N ha⁻¹ d⁻¹) and cumulative (g N ha⁻¹) values.

At the grassland site, N2O fluxes were also measured using the static closed chamber method with permanently installed collars. A photoacoustic multi-gas analyser (INNOVA 1412, Denmark) was connected to the two ports on the chamber (40 cm x 40 cm) using Teflon tubing. The tubes were 4 m long with a 3 mm inner diameter. The inlet and outlet of the photoacoustic connected to two ports on the top of the chamber. Ambient measurements were made for 30–40 minutes, until N2O readings had stabilized. For each chamber, five to six readings were taken over a four-minute period to calculate the flux. Two to four ambient readings were taken between different treatment plots. The limit of detection on the photoacoustic was 0.3 ppb.

After the first application, N2O was measured after three days and then every two to three weeks. Nitrous oxide fluxes were measured more frequently during the second and third growth periods: four days after slurry application and then at weekly or bi-weekly intervals. Comparison between the photoacoustic values for N2O and GC based determinations were in close agreement (r² > 0.95).

2.3 Calculation of N2O fluxes and emission factors
Fluxes were calculated as the increase in gas concentration within the chamber between the initial and final concentration using the following equation (de Klein and Harvey 2015):

\[
F = \frac{\Delta N_2O}{\Delta t} \times \frac{(MW \times P)}{(R \times T)} \times \frac{(V/A)}
\]

where:

\(\Delta N_2O\) is the change in concentration of N2O in the headspace volume (ppmv), \(\Delta t\) is the enclosure time period (minutes), MW is the molar mass of N2O-N (28 g), P is the atmospheric pressure at the time of sampling (Pa), R is the gas constant (8.314 J K⁻¹ mol⁻¹), T is the air temperature at the time of sampling (K), V is the headspace volume within the chamber (m³) and A is the area covered by the base (m²). Cumulative N2O fluxes were calculated using
trapezoidal integration with linear interpolation of flux values between two dates.

The $N_2O$ Emission Factors (EF) were calculated for the different N treatments using equation 2 below:

$$EF = \frac{(\text{Cumulative } N_2O-N_{\text{Fertilized}} - \text{Cumulative } N_2O-N_{\text{Control}}) / \text{Total N Applied}}{100}$$

(2)

where:

EF = Emission Factor ($N_2O-N$ emitted as a percentage of fertilizer applied), Cumulative $N_2O-N_{\text{Fertilized}}$ = Cumulative $N_2O-N$ fluxes for fertilizer treatments, Cumulative $N_2O-N_{\text{Control}}$ = Cumulative $N_2O-N$ fluxes for the control (N0) treatment, Total N Applied = N fertilizer application rate in kg N ha$^{-1}$.

### 2.4. Soil and climatic measurements

At the arable site, soil moisture or volumetric water content (VWC) was measured directly with a GS3 sensor probe and 220 handheld readout device (ProCheck, Decagon Devices, Pullman WA, USA). Soil temperature (°C) was measured with a hand-held digital thermometer (ELE International, Bedfordshire, UK). Measurements were made at a depth of 0–10 cm in the inter-row spacing adjacent to the collars.

At the grassland site, soil moisture and temperature (0–10 cm) were measured directly using a WET sensor (Delta-T Devices, Burwell, Cambridge, UK).

Water-filled pore space was calculated using the equation:

$$\text{WFPS} \% = \frac{\text{VWC}}{1 - \frac{\text{Bd}}{\text{Pd}}} \times 100$$

(3)

Where Bd is the soil bulk density (g cm$^{-3}$, 7 cm depth) and Pd is particle density estimated at 2.65 g cm$^{-3}$ (Linn and Doran 1984).

At the arable site, soil was sampled to a depth of 10 cm to determine soil ammonium ($NH_4^+$) and nitrate ($NO_3^-$) concentrations. Soil cores were taken weekly after fertilization for one month and then every three to four weeks until harvest. The soil samples were stored in a cold room with freezer blocks at 4 °C and extracted either on the same day of collection, or within 24 hrs, using 2 M KCL at a ratio of 5:1 (v:w) (Maynard et al. 2007). The $NH_4^+$ and $NO_3^-$ concentrations of the extract were analysed with an Aquakem 600 discrete analyser (Thermo Fisher Scientific, USA).

Climatic data for the arable sites was obtained from the Met Eireann automated weather station at Oakpark, Co. Carlow, Ireland; c. 750 m and 2 km from the 2014 and 2015 sites, respectively (Figure 1(a)). For the grassland site (c. 1 km away), climatic data was obtained from the Met Office automated weather station at Hillsborough, Co. Down, Northern Ireland (Figure 1(b)).

### 2.5. Statistical analysis

All analyses were conducted using SAS 9.4 (Cary, NC, U.S.A.). Normality and homogeneity of variance was checked using histograms and residual graphs. Where data was not normally distributed, log transformations were applied to improve the distributions. At
the arable site, tillage and nitrogen rate were the fixed effects with block and “block x tillage” set as the random effects. The effect of year was also included to examine variation between the two sites. At the grassland site, the main effects tested were treatment (control, NPK, slurry), fertilizer type (control, NPK, cattle, pig) and rate of application (control, NPK, 50, 100, 200) and their interaction with block as a random effect. Cumulative N$_2$O emissions and N$_2$O EFs was examined using the PROC GLIMMIX procedure, with significant pairwise differences determined according to the simulate post-hoc test (p < 0.05). Figures were made in Sigma Plot (v 14.0).

3. Results

3.1. Arable N$_2$O fluxes and EFs

In 2014, N$_2$O fluxes were quite low after the first N fertilizer application, with mean values ranging from −0.6 to 13.2 g N ha$^{-1}$ d$^{-1}$ for the CT treatments (Figure 2(a)) and 0.1 to 8.6 g N ha$^{-1}$ d$^{-1}$ for the ST treatments (Figure 2(b)). The temporal profile showed an abrupt increase in N$_2$O fluxes following the second application of fertilizer. This rise in N$_2$O production also corresponded with an increase in soil temperature. Peak N$_2$O flux occurred between the second and third fertilizer applications in all treatments, apart from the CT240 treatment (Figure 2(c)). The maximum daily N$_2$O fluxes were recorded in the CT240 (93.7 ± 6.7 g N ha$^{-1}$ d$^{-1}$) and ST320 (106.9 ± 21.6 g N ha$^{-1}$ d$^{-1}$) treatments. Nitrous oxide fluxes gradually decreased during April, corresponding to eleven consecutive days without rainfall (9$^{th}$-20$^{th}$ April). Fluxes of N$_2$O gradually decreased to background levels from May onwards.

In 2015, daily N$_2$O fluxes increased markedly in the higher N treatments after the second N fertilizer application (Figure 2(c,d)). The higher fluxes occurred when WFPS increased above 70% (Figure 3(c,d)) and soil temperatures > 10°C at the beginning of April (Figure 1(a)). These then gradually decreased during April between the second and third fertilizer applications across all N fertilized treatments, concurrent with decreases in WFPS (Figure 3(c,d)). The highest soil mineral N concentrations were also recorded during mid-April (Figure 3(a,b)). Pulsed N$_2$O fluxes were observed in the ST240 and ST320 treatments following rainfall (Figure 2(d)) and associated with an increase in WFPS (Figure 3(d)).

Nitrogen rate influenced the cumulative N$_2$O emissions (P < 0.0001, Table 1). In 2014, the mean cumulative N$_2$O emissions (CT and ST) were 3.1, 5.4 and 5.7 times greater in the 160, 240 and 320 kg N ha$^{-1}$ treatments, respectively, compared to the control treatments. Cumulative N$_2$O emissions were >1.7 times greater in the 240 and 320 kg N ha$^{-1}$ compared to the 160 kg N ha$^{-1}$ treatments. In 2015, higher cumulative N$_2$O emissions were recorded in the 240 and 320 kg N ha$^{-1}$ treatments, compared to the 160 kg N ha$^{-1}$ and control treatments. No significant differences in cumulative N$_2$O emissions were detected between the 240 and 320 kg N ha$^{-1}$ treatments in both seasons. There was no effect of tillage on the cumulative N$_2$O emissions with no significant differences between the CT and ST treatments for equal rates of applied N fertilizer. Averaged across sites, the mean cumulative N$_2$O emissions (all treatments) in 2015 (1.45 ± 0.20 kg N ha$^{-1}$) were only 67% of the values obtained in 2014 (2.15 ± 0.23 kg N ha$^{-1}$) (P < 0.0001, Table 1).
Generally, the CT EFs were < 1% and the ST EFs were ≥ 1% at the Oakpark site in 2014 (Table 1). The N₂O EF values were not affected by N rate whilst the effect of tillage was only marginally significant (P = 0.054, Table 1). In 2015, N rate influenced the EF values. Mean N₂O EF for the 240 kg N ha⁻¹ treatments (0.64%) was 4.4 times greater than the EF for the 160 kg N ha⁻¹ treatments (0.15%) (P < 0.05, Table 1). The mean N₂O EF in 2015 (0.46% ± 0.08) was 53% lower than the mean EF value in 2014 (0.87% ± 0.08).

![Figure 1](image.png)  
**Figure 1.** Daily rainfall and mean air temperature records from the automated weather stations at (a) Oakpark (01/08/2013 to 01/08/2015) and (b) Hillsborough (01/11/2015 to 01/12/2016).
3.2. Grassland \(N_2O\) fluxes and EFs

Soil temperature ranged from \(<10^\circ C\) from December to June, rising to maxima of between 24.4–26.4°C (3\textsuperscript{rd} June) and steadily declined from August to December (Figure 1(b)). Values for WFPS ranged from 30–91% across all treatments, averaging 57%, 63% and 62% for the first (T1), second (T2) and third (T3) growth periods, respectively (Figures 1, 4(a)).

Daily \(N_2O\) fluxes were quite low with values ranging from \(5.8 \pm 1.3 \text{ g N ha}^{-1} \text{ d}^{-1}\) to \(33.7 \pm 13.7 \text{ g N ha}^{-1} \text{ d}^{-1}\) (Figure 4(a)). In the T3 period, higher \(N_2O\) fluxes were recorded in the Cattle (H) (297.9 \pm 224.9 g N ha\(^{-1}\) d\(^{-1}\)) and Pig (H) (100.7 \pm 50.7 g N ha\(^{-1}\) d\(^{-1}\)) treatments four days after slurry application, and in the Cattle (M) (222.0 \pm 107.2 g N ha\(^{-1}\) d\(^{-1}\)), Cattle (H) (305.3 \pm 104.7 g N ha\(^{-1}\) d\(^{-1}\)) and Pig (H) (429.1 \pm 113.2 g N ha\(^{-1}\) d\(^{-1}\)) treatments six days after slurry application. These higher \(N_2O\) fluxes were associated with soil temperatures of 18.6–19.6°C at a WFPS of 70–82% (Figure 4(b,c)).

Cumulative \(N_2O\) emissions and EFs for the combined grass growth period (15\textsuperscript{th} March – 28\textsuperscript{th} September) are reported in Table 2. Across all treatments, the cumulative \(N_2O\) emissions ranged from 0.83 to 4.38 kg N ha\(^{-1}\). Fertilizer application rate significantly influenced the values obtained, and the cumulative \(N_2O\) emissions in the high-volume slurry application (200 m\(^3\) ha\(^{-1}\)) treatments were double those in the NPK, slurry (L) and slurry (M) treatments (\(P < 0.0001\)). The \(N_2O\) EFs were quite variable with values ranging from \(-0.70\% \pm 0.15\) to 0.49\% \pm 0.06 (Table 2). Fertilizer application rate also affected the EFs, where the mean value for the 200 m\(^3\) ha\(^{-1}\) treatments (Cattle and Pig) was significantly greater than the mean EF value for the 50 m\(^3\) ha\(^{-1}\) treatments (\(P < 0.001\), Table 2).

4. Discussion

4.1. Impact of tillage and N rate on \(N_2O\) fluxes

In the arable experiment (2014 & 2015), tillage had no effect on the cumulative \(N_2O\) emissions, when compared at equal rates of applied fertilizer (Figure 2(a-d), Table 1). This finding mirrors the results of Abdalla et al. (2010) who also found no effect of tillage on \(N_2O\) emissions from spring barley plots. In comparison, Chatskikh et al. (2008) observed significantly higher \(N_2O\) fluxes from direct-drilled (6.5 \pm 1.9 g N ha\(^{-1}\) d\(^{-1}\)) compared to a conventionally tilled (3.1 \pm 1.9 g N ha\(^{-1}\) d\(^{-1}\)) oilseed rape crop following N fertilizer application in spring. Due to the limited number of measurements made in their study it is, however, difficult to determine whether the annual cumulative \(N_2O\) emissions differed between the tillage treatments.

Nitrogen fertilizer applications generally stimulated higher \(N_2O\) fluxes (Figure 2(a-d)) but there was also a link with WFPS and soil temperature, with greater \(N_2O\) production at higher temperatures and higher WFPS. Žurovec et al. (2017) also reported higher \(N_2O\) fluxes in wetter (WFPS \(\geq\)71%), and warmer (>10°C) soils, presumably due to an increase in denitrification (Beauchamp 1997; Butterbach-Bahl et al. 2013). Warmer, wetter soils tend to increase the rate of denitrification in two ways. Firstly, greater oxygen consumption by microbes and roots increases the anaerobic volume in soil aggregates (Smith and Tiedje 1979; Schlüter et al. 2018) and, secondly, higher moisture levels act as a physical
barrier to gas diffusion, reducing soil oxygen concentrations (Cosentino et al. 2013; Smith 2017). The ensuing anaerobic/low oxygen conditions could then facilitate greater emissions of N$_2$O than would normally be found in aerobic soils (Rochette 2008).

Peak N$_2$O fluxes were generally observed at the beginning of April (Figure 2(a-d)). Keane et al. (2018) also reported large N$_2$O flux peaks in April of 478 g N ha$^{-1}$ d$^{-1}$ and 651 g N ha$^{-1}$ d$^{-1}$ in WOSR fertilized, with ammonium nitrate and ammonium only, respectively. They observed an increase in N$_2$O fluxes associated with higher levels of photosynthetically active radiation. Increased photosynthesis and the subsequent photosynthate supply provide labile C that could facilitate denitrifying activity leading to enhanced N$_2$O fluxes (Farquharson and Baldock 2008). Our maximum daily N$_2$O flux values of 107 and 100 g N ha$^{-1}$ (2014 and 2015) represented ≤22% of the values recorded in their experiment. As their chambers enclosed plants inside the chamber, as opposed to our soil-based chamber methodology, the result suggests a combination of plant mediated and environmental regulation on N$_2$O production in WOSR systems.

Interestingly, higher soil mineral N concentrations did not result in concomitant increases in N$_2$O fluxes (Figure 3(a,b)). This observation suggests that the uncultivated inter-row spacing of ST is occasionally susceptible to higher N$_2$O-N losses than conventionally tilled soils. A proportion of crop residue is retained in the inter-row

![Figure 2](temporal_n2o_fluxes.png)

**Figure 2.** Temporal N$_2$O fluxes in 2014 (left) and 2015 (right) for the CT plots at 125 mm row spacing (a, c) and ST plots at 600 mm row spacing (b, d) with (○, 160; ▼, 240; Δ, 320) or without (0, ●) fertilizer addition (kg N ha$^{-1}$). Vertical bars indicate standard errors of the daily mean fluxes ($n = 2$) and blue arrows (x-axis) indicate the date fertilizer was applied.
spacing, which may provide labile C substrate to support heterotrophic denitrification. Furthermore, mineralization of the N contained in residues can stimulate nitrification and/or denitrification processes depending on soil aeration status. However,
based on this evidence the extent of oxygen limitation (anaerobiosis) appears to strongly regulate N$_2$O fluxes at this site, and this is largely independent of soil mineral N availability.
Table 2. Cumulative N₂O emissions and EFs at the grassland site in Hillsborough.

| Treatment | Total N applied (kg N ha⁻¹) | N₂O (kg N ha⁻¹) | EF (%) |
|-----------|-----------------------------|----------------|--------|
| Control   | 0                           | 1.74 ± 0.23 a   | −0.02 ± 0.21ab |
| NPK       | 200                         | 1.70 ± 0.42 a   | −0.20 ± 0.35a |
| Cattle (L)| 160                         | 1.43 ± 0.56 a   | 0.28 ± 0.23ab |
| Cattle (M)| 320                         | 2.62 ± 0.75 a   | 0.43 ± 0.07b  |
| Cattle (H)| 640                         | 4.52 ± 0.44 b   | 0.49 ± 0.06b  |
| Pig (L)   | 130                         | 0.83 ± 0.19 a   | −0.70 ± 0.15a |
| Pig (M)   | 270                         | 1.69 ± 0.64 a   | −0.02 ± 0.24ab|
| Pig (H)   | 540                         | 4.38 ± 0.33 b   | 0.19 ± 0.06b  |

Type III ANOVA

| Treatment | Type | Rate | EF |
|-----------|------|------|----|
|           | n.s. | <0.001 | n.s. |
|           | n.s. | <0.001 | n.s. |

Different lowercase letters indicate a significant effect of rate on treatments within each column.

4.2. **Impact of long-term slurry application on N₂O fluxes**

Direct fluxes of N₂O from applied N were consistently low (<100 g N ha⁻¹ d⁻¹) for the majority of the measurement period. High N₂O fluxes were apparent only for the Cattle (M), Cattle (L) and Pig (H) treatments in the T2 growth period (Figure 4(a)). One explanation for the higher N₂O fluxes in July could be related to higher rates of denitrification. Like the arable experiment, the soil was warmer (>10 °C) and wetter later in the summer (July > May; ~20% WFPS). Using repacked soil cores, Maag and Vinther 1999 observed that denitrification losses at 72% WFPS accounted for 17 to 58% of the slurry's total N-NH₄⁺ content, but only 0.01 to 1.2% at 43 to 57% WFPS. Rafique et al. (2011) also found that N₂O fluxes from slurry were higher when applied to soils with high moisture contents. In addition, the pig slurry applied in July had 81–90% higher dry matter and 48–70% more total N (principally ammoniacal-N) than the slurry applied in March and May.

In addition to the effects of WFPS and soil temperature, the greater N₂O fluxes from the Cattle (M), Cattle (H) and Pig (H) treatments in the T3 period could be related to post cutting events (Figure 4). Rafique et al. (2012), for instance, observed increases in N₂O following cutting events in grasslands in the south of Ireland. Neftel et al. (2000) also reported higher N₂O fluxes after cutting, due to a reduction in plant uptake of NH₄⁺ and NO₃⁻. As slurry was applied the next day following cutting in the current experiments, mineral N was likely in excess of plant uptake leaving more soil N available for conversion to N₂O. Whilst a reduction in photosynthesis after cutting would likely have reduced the availability of C substrate for supporting denitrifying activity this may have been counterbalanced by C from decomposing plant root and shoot material.

Combining the three growth periods, greater cumulative N₂O-N losses were observed in swards receiving the highest cattle and pig slurry (H: 200 m³ ha⁻¹) applications (Table 2). Van Groenigen et al. (2004) also observed the greatest emissions of N₂O from high rates of cattle slurry applications (250 kg N ha⁻¹) to a clay soil. Applying a high volume of slurry after the grass was cut, combined with a higher WFPS and higher temperatures, was the possible cause of the greater
cumulative N\textsubscript{2}O emissions. Moreover, the absence of significant differences in N\textsubscript{2}O emissions between the urea (67 kg N ha\textsuperscript{−1}), 50 and 100 m\textsuperscript{3} ha\textsuperscript{−1} slurry treatments indicates greater plant utilization of applied N at lower application rates and that N\textsubscript{2}O emissions were more dependent on the amounts supplied rather than the fertilizer type.

4.3. Re-assessment of the Tier 1 EFs for Irish agricultural systems

In line with the cumulative N\textsubscript{2}O emissions, there were no significant differences in N\textsubscript{2}O EFs between the CT and ST treatments receiving the same rate of N fertilizer (Table 2). Abdalla et al. (2010) also found no significant difference in N\textsubscript{2}O fluxes for spring barley under conventional and reduced tillage, giving an overall EF of 0.6%. In their study, reduced tillage was carried out to a depth of 15 cm a practice that differs significantly from the type of reduced tillage used in this study. Strip tillage combines reduced tillage (cultivated plant rows) and no-tillage (uncultivated inter-row spacing’s). In this study, N\textsubscript{2}O fluxes were measured only in the inter-row spacing; implying that N\textsubscript{2}O EFs from ST may be even lower if N\textsubscript{2}O fluxes from the cultivated plant rows were accounted for at the field scale.

In their meta-analysis, Mei et al. (2018) calculated that the conservation tillage-induced N\textsubscript{2}O emission factor increased by 0.40% relative to conventional tillage. This value is similar to the average difference between the combined CT and ST cultivations in 2014 (0.65% and 1.09%), but less so in 2015 (0.33% and 0.58%). However, their comparative analysis of tillage regimes that included tropical (1.54%), warm temperate (0.15%) and cool temperate (0.08%) climates, the latter being representative of Irish conditions, found little tillage-related differences. Likewise, no significant tillage effect was observed at the two contrasting sites used in this study (Table 1), indicating that, for equal rates of N fertilizer, ST has a limited impact on N\textsubscript{2}O EFs.

Earlier studies in WOSR cropped soils have reported N\textsubscript{2}O EFs >50% lower than the IPCC default value of 1%. On sandy to silt loam soils, Vinzent et al. (2018) reported EFs ranging from 0.19–0.50% for WOSR over three seasons in Germany. Thers et al. (2019) also reported much lower EFs (0.28–0.36%) from mineral N applied to WOSR on a sandy loam soil in Denmark. Ruser et al. (2017) suggested an EF of 0.6% for WOSR at a fertilizer rate of 200 kg N ha\textsuperscript{−1}. With the exception of the ST treatment receiving 240 kg N ha\textsuperscript{−1} in 2014 (1.20%), the majority of values were considerably lower than the 1.27% EF value estimated in a meta-analyses of seven OSR sites across Europe (Walter et al. 2015). Merging our study with the current knowledge of WOSR cropping on N\textsubscript{2}O emissions, lower N\textsubscript{2}O EFs may be achieved under drier conditions (i.e. low WFPS) and/or where the crop is sown on soils with more porous textures.

Lower N\textsubscript{2}O EF values were attributed to potentially greater N uptake by plants at an N fertilizer rate of 160 kg N ha\textsuperscript{−1} (i.e. Knockbeg, Table 1). Across all treatments, the mean root biomass in 2015 (115 ± 2 g m\textsuperscript{−2}) was 1.8 times greater than the root biomass in 2014 (64 ± 7 g m\textsuperscript{−2}) (P < 0.0001, data not shown) for the same annual dates (3\textsuperscript{rd} March). Higher root biomass would have enabled greater fertilizer N uptake and reduced mineral N availability for microbial N\textsubscript{2}O production. The absence of over-winter grazing by woodpigeons in 2015 compared to the heavily
grazed crop in 2014 (Personal observation) also meant aboveground biomass was also considerably greater in 2015. As a result, the considerably lower cumulative N₂O emissions and EFs in 2015 could be associated with the larger canopy and sink capacity for N, in addition to the increased uptake of N fertilizer. However, to our knowledge, defoliation by herbivory during winter/spring and its potential effect on N₂O fluxes and total N₂O-N loss has not been examined for WOSR systems.

In addition, the N fertilizer application rates varied somewhat between years (Table S1). A greater amount of N was supplied in the second and third applications in 2014 (60, 100 and 140 kg N ha⁻¹) compared to 2015 (53, 80 and 106 kg N ha⁻¹) and this could also have contributed to the lower cumulative N₂O emissions in the first year.

Although the range of EFs found in the current study are generally within the range of previously reported values, the full annual cropping period was not accounted for; neither post-tillage nor post-harvest N₂O fluxes were measured. In WOSR cropped soils, elevated soil NO₃⁻ concentrations and the mineralization of crop residues may increase denitrification and subsequently N₂O fluxes (Kesenheimer et al. 2019). Ruser et al. (2017) suggesting that C availability for denitrifying communities, under conditions of non-limiting soil NO₃⁻, could be the main driver of post-harvest N₂O fluxes. The amount of residual N in the soil, the N uptake dynamics of the next crop and the prevailing climatic conditions will also influence post-harvest N₂O fluxes. Consequently, these factors would need to be considered in order to derive a comprehensive assessment of N₂O EFs associated with WOSR cultivation.

Nitrous oxide EFs from the grassland experiment also revealed large departures from the IPCC default value, ranging from −0.70 to 0.49% (Table 2). The presence of negative EFs on some occasions, often at the lower fertilizer/slurry applications, were due to the greater cumulative N₂O emissions from the unfertilized control. Whilst the reason for these results are not known the control plots had an altered species diversity compared to the majority of treatment plots and this may have, under some environmental conditions, decreased the uptake and/or utilization of soil N, leading to higher fluxes. At this site, Fornara et al. (2016) reported a higher root biomass in the control plots relative to those of the fertilized plots. Root exudates and/or enhanced root decomposition processes may have provided a significantly higher amount of labile C to soils, leading to higher N₂O fluxes from the control plots. In support of this is the fact that the control plots have continued to accumulate soil C since the experiment was established in 1970 (Fornara et al. 2016). Further studies would be required to examine the effect of different species diversity, increased root biomass and C substrate availability, in combination with a range of fertilizer treatments, in order to assess the underlying reasons for these results.

In this study, the slurry was spread by broadcasting, which may have given rise to proportionally higher NH₃-N fluxes (Lanigan et al. 2018). Also, the soil pH at the Hillsborough site ranged from 6.3 to 6.8 (data not shown) and, together with an increase in soil pH following slurry application, may have contributed to an increased NH₃:NH₄⁺ ratio (He et al. 1999) leading to greater ammonia volatilization, which could confound estimates of N₂O EFs. In an Irish grassland sward (>10 years), Bourdin et al. (2014) found NH₃ losses accounted for 30.3–70.8% of the applied cattle slurry. Misselbrook et al. (2000) also found NH₃ losses from cattle slurry equated to 59% of the total N applied on UK grasslands. Bourdin et al. (2014)
noted that NH₃ volatilization would effectively reduce the pool of soil mineral N available for microorganisms and impact on the measured EFs. Whilst default values for the fraction of N volatilized from organic manure (Frac_GASMi 19.7%) and indirect N₂O-N emissions (1% NH₃-N volatilized) are included in the IPCC inventory guidelines (IPCC 2019), a wide range of values have been reported. For this reason, the impact of NH₃ losses were not included in our analysis. Quantifying NH₃ fluxes directly would have provided more accurate EFs for slurry-treated grasslands (Bourdin et al. 2014).

A setback of using such high volumes of slurry also meant that the field was rendered inaccessible for short periods after slurry application. Chamber measurements lack temporal resolution (Khalil et al. 2020) meaning that large, but brief, N₂O flux peaks are often not captured (Butterbach-Bahl et al. 2013). Missing potentially high flux values likely caused cumulative N₂O emissions and N₂O EFs in the fertilized treatments to be underestimated. Additionally, a low temporal resolution in the control treatments could have led to an overestimation in the cumulative N₂O emissions. It may also be difficult to adequately capture spatial variability in the slurry-treated plots, due to unevenness in the spreading pattern and the thickness of the surface layer, unless a large number of replicates is used. The individual and/or combined effects outlined here may have contributed to the negative EF values obtained at the grassland site.

One way to reduce uncertainty when calculating cumulative emissions is to apply a Bayesian interpolation approach (Levy et al. 2017; Cowan et al. 2019, 2020). In this method, daily fluxes are interpolated by fitting values to a spatial log-normal distribution over time, i.e. a “peak-and-decay”, that characterizes the typical ecosystem response to N fertilizer input. Levy et al. (2017) compared numerous interpolation approaches and found that trapezoidal integration underestimated fluxes. A Bayesian approach may therefore produce more positive EF values with robust uncertainties, likely by estimating the “expected” peak N₂O fluxes constrained by low temporal/spatial resolution of the chamber measurements.

5. Conclusion

At the arable site, strip tillage did not increase cumulative N₂O emissions or EFs relative to conventional ploughing methods. Variation in plant growth was observed to influence EF values suggesting site-specific information, in addition to management practices, is required to generate robust N₂O EF inventories for oilseed rape and other crops. At the grassland site, significantly more N₂O was emitted from plots receiving cattle and pig slurry at a rate of 200 m³ ha⁻¹. The wide range in observed N₂O EFs signals the need for site-specific values that incorporate fertilizer rate and type for grassland ecosystems. Future studies that incorporate a longer N₂O measurement campaign across multiple sites, replicated over annual timescales, with sampling conducted at higher temporal resolutions, will help to refine the N₂O EF estimate for mineral/organic fertilizer applied to arable/grassland soils.
Article highlights

- Nitrous oxide fluxes and emission factors were quantified for an arable and a grassland ecosystem.
- In the arable system, \( N_2O \) EFs ranged from 0.03% to 0.87% for conventional tillage and 0.26% to 1.20% for the strip tillage systems.
- In the grassland system, annual \( N_2O \) EFs ranged from −0.70% to 0.49%, with the low/negative values often associated with the lower fertilizer applications.
- Differences in the EFs from the two arable sites were associated with site-specific effects (2014) and nitrogen application rate (2015), rather than tillage practice.
- These results argue for a more detailed quantification of land-use related EFs and how they are influenced by site and management-related factors.

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ORCID

M. O'Neill http://orcid.org/0000-0003-0249-967X

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