



Effect of slurry dry matter content, application technique and timing on emissions of ammonia and greenhouse gas from cattle slurry applied to grassland soils in Ireland



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ABSTRACT

Agriculture contributes to 98% and 33% of ammonia and greenhouse gas (GHG) emissions in Ireland, respectively. Those emissions are mainly associated with livestock production. The Gothenburg Protocol and the EU National Emissions Ceilings Directive are policy drivers which set new and more demanding targets from 2020 to reduce these gaseous emissions. A field experiment was set up in Wexford (Ireland) between April 2009 and August 2010, on a grassland site established with a uniform ryegrass (*Lolium perenne*) sward for more than ten years. The objective was to investigate the impact of slurry dry matter (DM) content, application technique and timing of application on the overall GHG balance from cattle slurry applied to grassland soils. The treatments on plots were a control, calcium ammonium nitrate (CAN) and cattle slurry, either grass-based or maize-based and with varying DM contents, applied by mimicking trailing shoe and splash plate application. The dry matter contents were varied by mixing different ratios of faeces and urine. The results showed that, while ammonia (NH₃) volatilisation losses were significantly increased on slurry spread plots, cumulative direct nitrous oxide emissions, and corresponding emission factors, were significantly higher when applying CAN. In terms of GHG field balance, the potential decrease in indirect nitrous oxide (N₂O) emissions, calculated from a reduction of ammonia volatilisation losses using trailing shoe as opposed to splash plate, could be easily offset by an increase in direct N₂O emissions and ecosystem respiration. Switching from summer to spring application was much more efficient for mitigation of both NH₃ and GHG emissions, due to favourable soil and climatic factors which enhanced crop growth. Any potential trade-off between NH₃ and N₂O emissions was cancelled, leading to an overall positive effect on reactive nitrogen losses and offering agronomic benefits to farmers.

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1. Introduction

Agriculture in Ireland is the main source of ammonia (98% of NH₃ emissions) and contributes to 33% of greenhouse gas (GHG) emissions with the majority of these associated with livestock production (Duffy et al., 2013).

Ireland is a Party to the Convention on Long-Range Transboundary Air Pollution (CLRTAP, also known as “Gothenburg Protocol”), under which certain transboundary air pollutants (including NH₃) are targeted for control (UNECE, 1999). As a member of the European Union (EU), the country is also subject to the National

Emission Ceilings (NEC) Directive (EU, 2001), which implements the Gothenburg targets for member states. Target emissions for Ireland to be achieved by 2010, under the NEC Directive, were 116 kt (Humphreys, 2008). NH₃ emissions reached 130 kt in 1998 but declined to 113 kt in 2005, because of a smaller ruminant livestock population and reduced use of fertiliser nitrogen (N). However, both the Gothenburg Protocol and the EU National Emissions Ceilings Directive were reviewed with a new target of 0.5% reductions on 2005 levels by 2020 (DAFM, 2013).

NH₃ emissions from manure spreading to land contribute about a third of the total N emissions from agriculture in industrial countries (Misselbrook et al., 2000). Hyde et al. (2003) estimated that spreading of cattle slurry on grassland is the source of approximately 25% of NH₃ emissions in Ireland. Therefore, there is a need to develop NH₃ abatement strategies to reduce volatilisation losses when applying cattle slurry to grassland. This can be achieved by modifying the method of slurry application as well as optimising

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the timing of application or modifying slurry characteristics (Brink et al., 2001). However, reduced NH_3 losses from manure spreading are likely to increase N availability in agricultural soils and this may, in turn, affect the production and release of nitrous oxide (N_2O) (Brink et al., 2001). As N_2O is a potent GHG with a global warming potential 298 times that of carbon dioxide (CO_2) (IPCC, 2007), this could be regarded as pollution swapping (Stevens and Quinton, 2009) where attempts to abate the release of one ecologically harmful gas result in an increase in the emissions of another.

In Ireland, N_2O represented, in 2011, 13% of national GHG emissions and 40% of GHG emissions from agriculture. Manure management accounted for 6% of those emissions while N_2O sourced from manure application to land comprised 9% of agricultural N_2O emissions and 24% of direct N_2O emissions from agricultural soils (Duffy et al., 2013).

Methane (CH_4) is another potent GHG, with a global warming power 25 times that of CO_2 (IPCC, 2007), which represented 20% of national GHG emissions and 60% of GHG emissions from agriculture (Duffy et al., 2013). Those CH_4 emissions have decreased since 1998 mainly as a result of lower CH_4 losses from enteric fermentation which was a consequence of a gradual reduction in sheep numbers. Hence CH_4 from manure management has remained relatively static over the same period (Duffy et al., 2013).

Under the Kyoto Protocol (UNFCCC, 1997), Ireland was limited to an increase in GHG emissions by 13.5% for the period 2008–2012 (relative to 1990 levels). Whilst these emissions are just on target, the country has been set, under the EU 2020 Climate and Energy Package and its associated Effort-Sharing Decision, a further 20% reduction target for its non-Emission Traded Sectors (EU, 2009). As agriculture comprises over 40% of this category of emissions, there will be sustained pressure into the future to reduce GHG emissions.

Research on abating NH_3 emissions from manure spreading has primarily focused on comparing the NH_3 and N_2O emissions from surface (conventional or band spreading) and injection application methods (e.g. Weslien et al., 1998; Sistani et al., 2010; Velthof and Mosquera, 2011). Injection methods have been shown to reduce NH_3 volatilisation losses up to 90% (Dendooven et al., 1998) but they can also lead to an increased release of N_2O from soils in the weeks following slurry application (Wulf et al., 2002; Velthof and Mosquera, 2011). However, observations of this increase in N_2O emissions are inconsistent and some studies report no effect of application technique (Dendooven et al., 1998; Weslien et al., 1998). Sistani et al. (2010) also showed contrasted results, when comparing both surface application and injection of swine effluent, as they observed lower N_2O emission from injected plots during the first year of their experiment, but they found higher emissions from the same plots in the second year.

Trailing-shoe application of slurry to grassland soils has been shown to be an efficient NH_3 abatement technique (Misselbrook et al., 2002); it is considered to be the most effective way to lower NH_3 losses for many grassland areas, especially where a high stone content of soils and undulating topography make injection unsuitable. However, only a few studies have compared N_2O emissions from low trajectory slurry applications (e.g. with a trailing-shoe) with those from the broadcast method.

Timing of manure application affects NH_3 emissions as they increase with temperature and wind speed (Sommer et al., 2003). Timing is also likely to affect N_2O emissions since N_2O production is mainly driven by N availability, temperature and soil aeration, which vary temporally. Most studies investigating the impact of timing of slurry applications on NH_3 and N_2O emissions have focused on comparing autumn and spring applications, as reviewed by VanderZaag et al. (2011). However, slurry in Ireland is applied mainly in the summer (Hyde and Carton, 2005) when N volatilisation losses are likely to be enhanced by higher soil temperatures. Spreading of slurry in the spring is restricted if soils remain above

field capacity and rates of infiltration are low, even although uptake by herbage is high and lower soil temperatures reducing volatilisation losses. However, after applying pig and dairy slurries onto perennial ryegrass, Chadwick et al. (2000) observed higher N_2O losses in spring than in summer suggesting that, while spring application may reduce NH_3 losses to the atmosphere, this may be offset by higher N_2O emissions.

One possible way to reduce NH_3 volatilisation from spreading of manures could be by dilution. NH_3 fluxes have been shown to increase with increasing dry matter (DM) content in liquid manures (Sommer and Olesen, 1991). A higher content of solids can lead to sealing of soil pores, reducing the rate of infiltration into the soil and potentially increasing NH_3 volatilisation (Donovan and Logan, 1983; Dosch and Gutser, 1996). Sommer and Olesen (1991) observed that dilution of slurry from 12% to 4% DM content could reduce NH_3 losses. Mkhabela et al. (2009) showed similar results on NH_3 losses after diluting swine slurry and investigated the effect of such dilution on N_2O losses post-application, finding no significant effect of slurry dilution. Gregorich et al. (2005) found that N_2O emissions from liquid manure application were increased up to three fold compared to solid manures, with a much larger N fraction lost as N_2O .

The objective of this study was to investigate the impact of slurry application technique and timing of application, as well as the influence of slurry type (defined by parameters such as its DM and N content or its C:N ratio), on the overall GHG balance from cattle slurry applied onto grassland soils. The hypotheses formulated for this experiment are:

- Any reduction in NH_3 losses, following an alteration of slurry DM content, a switch from splash-plate to trailing-shoe or from summer to spring/autumn application will increase soil N pools, leading to an increase in measured N_2O emissions (as a result of the trade-off between NH_3 and N_2O fluxes).
- The supply of extra N to the soil (following the implementation of one of the NH_3 abatement strategies tested in this experiment), coupled with an input of organic carbon (C), will enhance soil microbial activity, increasing soil (and ecosystem) respiration.

2. Materials and methods

2.1. Site characteristics

The experiment was undertaken between April 2009 and August 2010, on a grassland site in Johnstown Castle, Wexford, Ireland (52°18'N; 6°30'W). The field is under an established (>10 years) and uniform ryegrass (*Lolium perenne*) sward. The mean annual rainfall and temperature, averaged over 25 years (Rosslare weather station, Met Eireann, 1978–2003), are 1044 mm and 10 °C, respectively. The soil is a well-drained coarse loam over fine loam, classified as a Haplic Cambisol Brown Earth. Some characteristics of the topsoil are given in Table 1. Prior to the experiment, a 180 m² area was divided into 40 plots (2 m × 1.5 m, 0.5 m gap between each) (Fig. 1).

2.2. Soil measurements and analyses before experiment

In March 2009, before applying any treatment on the plots, soil samples ($n = 10$) were collected from the field (Fig. 1), at two different depths (0–10 and 10–20 cm).

Total C and N contents of soil were analysed using a LECO TruSpec CN analyser (LECO Corporation, St. Joseph, MI, USA). Prior to the analysis, the soil samples were wet sieved to 2 mm, frozen at –80 °C for 16 h, freeze dried for 48 h and finally ground into fine powder. Ammonium nitrogen ($\text{NH}_4^+\text{-N}$) and Total Oxidised

Table 1
Particle size distribution, pH, C and N content of the first 20 cm of soil in the experimental site (data collected in March 2009 and expressed as mean values \pm standard errors).

Layer (cm)	% Clay	% Silt	% Sand	pH	% C	% N	C:N
0–10	13.9 \pm 1.2	29.0 \pm 1.6	57.1 \pm 4.8	5.5 \pm 0.1	3.02 \pm 0.18	0.30 \pm 0.02	9.92 \pm 0.32
10–20	14.7 \pm 1.5	29.1 \pm 1.9	56.2 \pm 5.1	5.4 \pm 0.1	2.08 \pm 0.35	0.23 \pm 0.04	9.21 \pm 0.17

Nitrogen (TON) fractions were determined by extracting 5 g of fresh soil with 50 ml of a solution of 2 M potassium chloride (KCl) (Maynard and Kalra, 1993). The gravimetric soil moisture content of the soil was measured by drying 10 g of field-moist soil overnight at 105 °C.

To get an average value for the dry bulk density of the field site, intact soil cores ($n = 10$) of known volume (251.33 cm³) were collected at a depth of 10 cm at the sampling points shown in Fig. 1 using a soil sample ring kit (Eijkelpamp, Em Giesbeek, The Netherlands).

In the laboratory, samples were weighed moist, dried overnight at 105 °C and then weighed again before calculation of gravimetric soil moisture content. Sample bulk density was calculated as the mass of oven-dry soil divided by the volume of the sampling cylinder. For each sample, dry soil was then sieved through a 2 mm sieve and the stones left on the mesh were weighed. As the mass of stones never exceeded 5% of the total sample weight, calculated sample bulk density was used as an approximation of soil dry bulk density for each sample.

2.3. Treatment application and slurry analyses

In 2009, 21 plots were set out in a randomised block design ($n = 3$) (Fig. 1). Twelve plots were spread with cattle slurry, either

grass-based or maize-based and with varying dry-matter contents (Table 2). Slurry was applied using a watering can fitted with a steel nozzle shaped to mimic a splash plate. When spreading slurry with the watering can, the nozzle was kept about 50 cm above the ground, at a similar height the splash plate would stand above the ground in the traditional broadcast application process.

In addition, another three plots were spread with low DM content maize-based slurry, using a watering can without a nozzle but according to a typical trailing shoe pattern of application. Slurry was deposited in a line, directly onto the ground and through the grass canopy to reduce its subsequent exposure to ambient air.

The different slurry treatments used in this experiment were prepared directly on the field by mixing thoroughly given proportions of faeces (1/3–1/5 of the prepared volume of slurry) and urine in a plastic bucket. The resulting slurry was then poured in to a watering can and applied to the plots.

Slurry applications were carried out on four separate dates (24 April, 20 July, 17 August and 20 September 2009) to provide a range of contrasting weather conditions. Spreading occurred at approximately midday on each occasion, at a rate of 30 t ha⁻¹. This represented a N supply rate from 26.1 up to 35.7 kg N ha⁻¹ per application for low DM content slurries, and from 60.3 up to 67.2 kg N ha⁻¹ for high DM content slurries. The reason for using difference N content between low and high DM content slurries is to observe the effect of varying N content on nitrogenous gas emission such as N₂O and NH₃. The carbon (C) application rate ranged from 380 to 646 kg C ha⁻¹ and from 836 to 1022 kg C ha⁻¹ per application for low and high DM content slurries, respectively (Table 2).

Formulated slurries were directly sampled in the field, after mixing urine and faeces and prior to application. They were then stored in the cold room for subsequent analysis. Slurry DM content was calculated by the difference in weight before and after drying fresh slurry at 105 °C for 24 h. Total C and N content of slurry were analysed as described in Section 2.2, except that frozen slurry samples were freeze-dried for 120 h.

The experiment also included control plots (no N applied) and plots fertilised with calcium ammonium nitrate (CAN) at a rate of 60 kg N ha⁻¹. A granulated form of CAN was applied by hand on the same dates slurry treatments were applied.

2.4. Measurements of gaseous emissions from the soil

2.4.1. Soil carbon dioxide measurements

Soil CO₂ respiration was measured at 30 s intervals using an EGM-4 infra-red gas analyser (PP Systems, Hitchin, Herts, UK) set to absorb radiation at 426 nm and coupled to a closed chamber with sampled air being sucked from the chamber to the analyser and recycled back to the chamber after analysis. Two rubber septa were inserted at the top of the chamber and air circulated between the chamber and the analyser using a flexible tubing system. The CO₂ flux was calculated from the increase in the concentration of CO₂ inside the chamber integrated over the sampling period.

Measurements were taken for a period of 3 min on each plot. During the measurement period, air was pumped at a rate of 500 ml min⁻¹ from the chamber to the CO₂ analyser. The chambers (11.3 cm in diameter and 16.3 cm high) were inserted to a depth of 2 cm into the soil to give a nominal 1434 cm³ air volume in the chamber. Each chamber was randomly positioned on its corresponding plot, except for trailing-shoe applied plots where

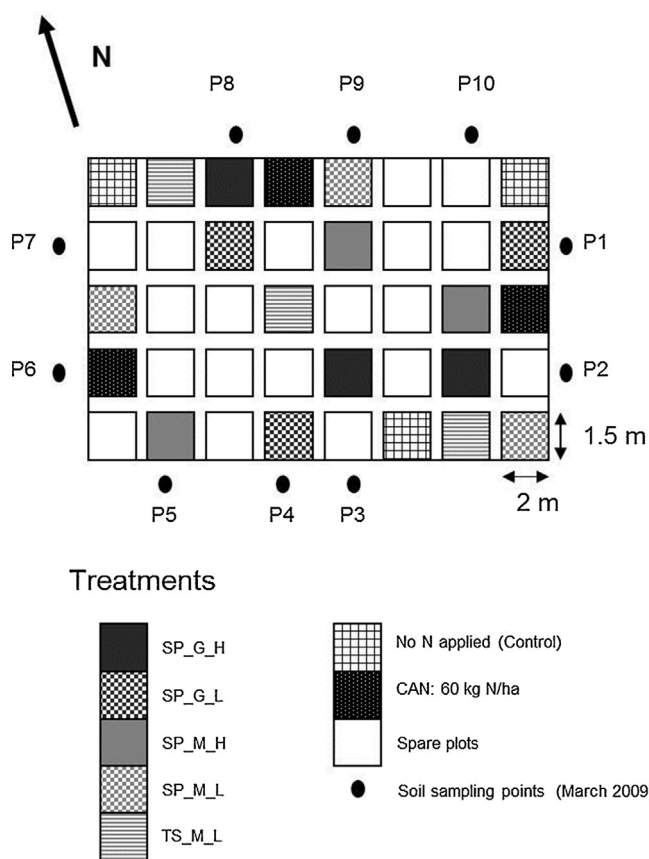


Fig. 1. Experimental design for the four slurry application in 2009. Soil characteristics before experiment were determined at sampling points P1 to P10. Soil samples ($n = 10$) were collected from the field at two different depths (0–10 and 10–20 cm).

Table 2

Characteristics of slurry treatments applied in (a) April, (b) July, (c) August and (d) September 2009.

Treatment	DM content (% total weight)	N content (g kg ⁻¹ fresh slurry)	C:N ratio	N application rate (kg ha ⁻¹)	C application rate (kg ha ⁻¹)
(a)					
SP.G.H	7.40	2.17	12.6	65.1	836
SP.G.L	3.81	1.13	14.7	33.9	496
SP.M.H	7.32	2.75	10.5	82.5	863
SP.M.L	3.98	1.09	16.0	32.7	525
TS.M.L	4.45	1.20	16.3	36	588
(b)					
SP.G.H	7.42	2.10	15.6	63.0	985
SP.G.L	3.79	1.15	14.0	34.5	482
SP.M.H	7.60	2.08	16.4	62.4	1022
SP.M.L	4.26	1.19	16.1	35.7	575
TS.M.L	4.79	1.31	16.4	39.3	646
(c)					
SP.G.H	5.28	2.24	13.2	67.2	887
SP.G.L	2.06	0.87	15.9	26.1	416
SP.M.H	6.01	2.18	13.8	65.4	904
SP.M.L	3.29	1.12	14.1	33.6	475
TS.M.L	3.47	1.22	15.3	36.6	559
(d)					
SP.G.H	6.50	2.01	14.6	60.3	882
SP.G.L	2.88	1.13	15.3	33.9	518
SP.M.H	6.34	2.17	15.1	65.4	985
SP.M.L	2.51	1.13	13.8	33.9	468
TS.M.L	2.48	0.89	14.2	26.7	380

Note: SP.G.H, splash plate-grass-based cattle slurry-high DM; SP.G.L, splash plate-grass-based cattle slurry-low DM; SP.M.H, splash plate-maize-based cattle slurry-high DM; SP.M.L, splash plate-maize-based cattle slurry-low DM; TS.M.L, trailing shoe-maize-based cattle slurry-low DM.

the chamber covered the slurry band for about 1/3 of the sampling area as long as such band was visible on the field.

CO₂ fluxes (in g CO₂-C m⁻² s⁻¹) were calculated from the six measurements made over the sampling period, using the following equation:

$$F_{\text{CO}_2} = \frac{PM_{\text{CO}_2}}{RTM_C} \frac{V}{A} \frac{\Delta C_{\text{CO}_2}}{\Delta t} \times 10^{-6} \quad (1)$$

where P is the air pressure inside the chamber (calculated by the analyser, in atmospheres), M_{CO_2} is the molar mass for CO₂ (44.01 g mol⁻¹), M_C is the standard atomic weight for C (12.01 g mol⁻¹), R is the gas constant (8.205746 × 10⁻⁵ m³ atm K⁻¹ mol⁻¹), T is the air temperature at the grass level (measured at Johnstown Castle weather station, in K), V is the volume of the chamber (in m³), A is the area covered by the chamber (in m²) and $\Delta C_{\text{CO}_2}/\Delta t$ is the slope given by the linear regression of the concentration of CO₂ inside the chamber over the measuring period (in ppm s⁻¹).

Flux estimates were processed as obtained or converted to kg CO₂-eq ha⁻¹ day⁻¹ for subsequent statistical analysis.

Measurements were taken between 1000 and 1300 h daily for the first 10 days, and then weekly. Gaseous fluxes were monitored weekly (or fortnightly) during October 2009, and then monthly from November 2009 to March 2010. At the start of the new growing season, fluxes were measured fortnightly until August 2010.

2.4.2. Nitrous oxide and methane measurements

N₂O and CH₄ fluxes were made using closed static chambers (Smith et al., 1995). The flux is calculated from the increase in concentration of the targeted gas inside the chamber.

The same chambers than in the CO₂ measurements were used, with the same criteria for its positioning on trailing-shoe applied plots. Rubber septa, previously removed to avoid over pressurisation inside the chamber, were rapidly put in place at the top of the chamber. Each chamber was randomly positioned on its corresponding plot.

Ambient air samples were collected at time zero and then from the closed chamber after 40 min. Samples were taken using a 20-ml gas-tight polypropylene syringe (BD Plastipak, Becton Dickinson, Spain), opened fully and fitted with a hypodermic needle. To collect a sample from a chamber, the needle was inserted through the septum and the syringe flushed to ensure adequate mixing of the air within the chamber prior to the withdrawal of a sample. The sample was then immediately injected into a pre-evacuated 7-ml gas-tight vial (Supelco, Bellefonte, PA, USA).

Measurements were taken usually between 1400 and 1700 h, daily for the first 10 days, and then weekly. Gaseous fluxes were monitored weekly (or fortnightly) during October 2009, monthly from November 2009 to March 2010, and then every two weeks until August 2010.

The N₂O and CH₄ concentration in each sample was analysed using a gas chromatograph (GC) (Varian CP 3800 GC, Varian, USA) fitted with a 3.75 m packed column (Poraplot Q packed column, JVA Analytics, Dublin, Ireland). From each vial a 0.7 ml sub-sample was automatically injected into the chromatograph using a Combi-Pal automatic sampler (CTC Analysis, Switzerland) under computer control. The N₂O concentration was analysed using an Electron Capture Detector (E.C.D.) at 300 °C while a Flame Ionisation Detector (F.I.D.) was used to detect CH₄.

Nitrous oxide (in g N₂O-N m⁻² h⁻¹) and CH₄ fluxes (in g CH₄-C m⁻² h⁻¹) were then calculated using the following equations:

$$F_{\text{N}_2\text{O}} = \frac{PM_{\text{N}_2\text{O}}}{RTM_N} \frac{V}{A} \frac{\Delta C_{\text{N}_2\text{O}}}{\Delta t} \times 10^{-9} \quad (2)$$

$$F_{\text{CH}_4} = \frac{PM_{\text{CH}_4}}{RTM_C} \frac{V}{A} \frac{\Delta C_{\text{CH}_4}}{\Delta t} \times 10^{-9} \quad (3)$$

where P is the atmospheric pressure (taken from Johnstown Castle weather station, in Pa), $M_{\text{N}_2\text{O}}/M_{\text{CH}_4}$ is the molar mass for N₂O (44.013 g mol⁻¹) or CH₄ (16.04 g mol⁻¹), M_N/M_C is the standard atomic weight for N (14.07 g mol⁻¹) or C (12.01 g mol⁻¹), R is the gas constant (8.314472 m³ Pa K⁻¹ mol⁻¹), T is the air temperature at the grass level (as reported by Johnstown Castle weather station,

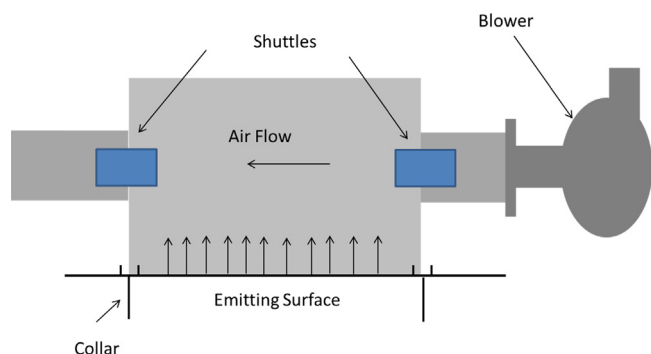


Fig. 2. Schematic of the NH_3 measuring apparatus.

in K), V is the volume of the chamber (in m^3), A is the area covered by the chamber (in m^2) and $\Delta C_{\text{N}_2\text{O}}/\Delta t$ (or $\Delta C_{\text{CH}_4}/\Delta t$) is the variation of gas concentration over the measuring period (ppb h^{-1}).

Flux estimates were converted either to $\text{kg N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ ($\text{kg CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$) or to $\text{kg CO}_2\text{-eq ha}^{-1} \text{ day}^{-1}$ for subsequent statistical analysis. The global warming potential (GWP) of each gas for a 100 year time horizon (IPCC, 2007) was used for the final conversion, with the following values: $\text{GWP}_{\text{CH}_4} = 25$ and $\text{GWP}_{\text{N}_2\text{O}} = 298$.

Emission factors for N_2O were calculated for each treatment using the following equation:

$$EF = \frac{F_{\text{N}_2\text{O}} (\text{Treatment}) - F_{\text{N}_2\text{O}} (\text{Control})}{N_{\text{Applied}} - F_{\text{NH}_3} (\text{Treatment})} \quad (4)$$

where $F_{\text{N}_2\text{O}}$ and F_{NH_3} refers to cumulative fluxes of N_2O and NH_3 , for the entire experimental period, integrated from measurements on control or treated plots; and N_{Applied} refers to the total amount of N applied on corresponding treated plots.

2.4.3. Ammonia measurements

Ammonia measurements were made using open dynamic chambers constructed from poly-vinyl chloride ($40 \text{ cm} \times 40 \text{ cm}$), with NH_3 concentration measured at the inlet and outlets of the chambers. Each chamber had a centrifugal air blower (95 CFM Active Air blower, Hydrofarm Ltd., USA) with airflow regulated at 15 L min^{-1} through each chamber. The blower was connected to the chamber by means of 10 cm diameter air conditioning ducting (Ferns Engineering, Wexford). Prior to entering each chamber, NH_3 contained in the ambient air was sampled using a Leuning sampler placed in series with the chamber (see Fig. 2). Each sampler consisted of a stainless steel sheet coated with oxalic acid (3%) crystals coiled inside a cylindrical plastic body (Leuning et al., 1985). Another set of samplers was placed after the outlet. Airspeed through the chamber was monitored using hot wire anemometers (RS 1340, Radionics, Rialto, Dublin) placed inside the chamber outlets and airflow was modulated by varying airflow from the air blowers. External windspeed was monitored using a Gill R3 sonic anemometer (Gill Instruments, Lymington, UK) and chamber airflow varied to match this by altering blower flow rate. Fluxes were subsequently calculated as the difference between the inlet and outlet NH_3 concentration, accounting for the mass flow of air across the chamber per time unit. Ammonia samplers were replaced after 1, 2, and 6 h. Chambers were removed and replaced for a 12 h period after 6, 24, 72 and 144 h. Calculations were validated against ALFAM modelled outputs (Sogaard et al., 2002, Fig. 3, $R^2 = 0.94$).

Indirect N_2O emissions, resulting from the N volatilised from the experimental plots being redeposited in another place, within a two kilometre radius, and reemitted as N_2O , were calculated using a default value of 1% of measured $\text{NH}_3\text{-N}$ being converted into an indirect N_2O flux to be accounted into the field-scale greenhouse gas budget (IPCC, 2006).

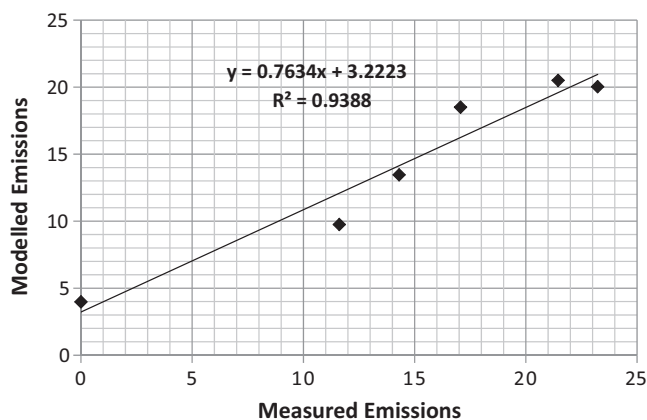


Fig. 3. Correlation between NH_3 measurements and output of the ALFAM model.

2.5. Monitoring of soil and weather parameters during experiment

Throughout the period of the study, the meteorological station in Johnstown Castle reported the hourly rainfall, soil temperature, wind speed and solar radiation. The recorded air pressure (P) and temperature at the grass level (T) were used in the calculation of trace gas fluxes, as shown in the Eqs. (1)–(3) (see Sections 2.4.1 and 2.4.2).

For many of the soil CO_2 measurements or gas sampling days, soil temperature and soil volumetric water content were measured outside the chambers, about 5 cm apart from the chamber wall, after inserting a sensor (WET-1, Delta-T Devices, Cambridge, UK), connected to a data logger (HH2 Moisture Meter, Delta-T Devices, Cambridge, UK), into the top 10 cm of soil. Measurements were taken for each plot immediately after measuring the CO_2 efflux or while sampling for CH_4 and N_2O determinations.

However, due technical issues, values for soil temperature and moisture content were either missing or discarded before the second slurry application in July 2009. For the same reasons, those values were missing on a few other gas sampling events. As a consequence, those measured soil data were rather considered as factors, when investigating the effect of environmental parameters on trace gas fluxes (see Section 2.4.3) than used to correct those fluxes for soil temperature variability.

Water filled pore space (WFPS, in %) was calculated as follow (Franzuebbers et al., 1999):

$$\text{WFPS} = \frac{\theta \cdot D_p}{1 - (D_B/D_p)} \quad (5)$$

where θ is the soil volumetric content (in %), D_B is the soil dry bulk density (see Section 2.4, in g cm^{-3}) and D_p is the soil particle density (in g cm^{-3}). For the purpose of this study, the average value for mineral soils (2.65 g cm^{-3}) was used in WFPS calculation.

2.6. Statistical analysis

Data were analysed using the statistical package STATISTICA version 10 (Statsoft, Tulsa, Oklahoma).

Estimates of cumulative flux were analysed using either a one-way Analysis of Variance (ANOVA) to investigate the differences between inorganic fertiliser (CAN) and cattle slurry spread plots in terms of gaseous emissions from the field plots, or a factorial ANOVA to explore the effect of slurry type, application technique or DM content on NH_3 and GHG emissions. In the latter case, a nested design was used to take into account the imbalance of the experimental design. The impact of timing of application was investigated using a Repeated Measures ANOVA with four levels of repetition

Table 3

Cumulative gaseous fluxes integrated from field measurements over the entire experiment (428 days) and expressed per amount of total N applied. Fluxes are expressed as mean values \pm standard errors.

	N ₂ O direct (% N applied)	N ₂ O indirect ^a (% N applied)	CO ₂ (kg CO ₂ -C kg ⁻¹ N applied)	CH ₄ (kg CH ₄ -C kg ⁻¹ N applied)	Total GHG (kg CO ₂ -eq kg ⁻¹ N applied)
CAN	1.75 \pm 0.78	0.03 \pm 0.01	26.09 \pm 1.82	0.01 \pm 0.00	104 \pm 4
Slurry	0.67 \pm 0.05	0.49 \pm 0.03	42.85 \pm 2.99	0.02 \pm 0.00	163 \pm 11

^a Note: Indirect N₂O-N emissions = 1% of volatilised NH₃-N losses (IPCC, 2006).

corresponding to the four application dates. In the three types of analysis, differences between individual treatments were assessed using Least Significant Difference (Fisher LSD test, $\alpha = 0.05$).

Due to the structure of the data, non-parametric statistics were used in some occasions. Indirect N₂O emissions from CAN and slurry spread plots were compared using a Mann–Whitney test on cumulative fluxes per unit of N applied. Whenever the use of a Repeated Measures ANOVA was not possible, a Friedman test was performed to analyse the effect of timing of application.

Non-parametric Spearman rank correlations were calculated to assess the effect of soil and weather parameters on measured N₂O fluxes and ecosystem respiration, whenever those environmental data were available.

3. Results

3.1. Comparison between mineral fertiliser and cattle slurry over the entire experiment

The quantity of NH₃ volatilised over the entire experiment (428 days from the 24th April 2009 to the 30th June 2010) was significantly higher ($P < 0.0001$, square root-transformed data) for the plots with slurry additions compared to both controls and plots fertilised with CAN (Table 3). NH₃ losses via volatilisation post slurry application, which amounted for 38.3–70.8% of the total N applied, were 11–16 times higher than for plots fertilised with only CAN. NH₃ losses from CAN fertilised averaged 2.9% of the applied N and were not significantly different from those measured for control plots.

By contrast, plots applied with slurry had significantly lower direct N₂O emissions ($P < 0.0001$, log-transformed data) than plots fertilised with CAN (Table 4). Mean direct N₂O emissions following slurry application represented only 1.4% of the total N emissions to atmosphere (38% for CAN plots).

Slurry application also increased CO₂ emissions from the soil ($P < 0.005$), while CH₄ emissions from the various treatments were generally lower than other GHG emissions (Table 4). The total amount of GHG emitted from the plots (in kg CO₂-eq ha⁻¹), accounting for N₂O, CO₂ and CH₄ emissions directly measured on site, as well as for off-site indirect N₂O emissions estimated from NH₃ data measured on-site (see Section 2.4.3) was significantly ($P < 0.005$) higher for slurry spread plots, compared to controls, but there was no significant difference between slurry and CAN treatments. However, once expressed per amount of total N applied, GHG emissions emitted from the soil (in kg CO₂-eq ha⁻¹ kg⁻¹ N applied) after slurry application were on average 57% higher than those following CAN additions (Table 3), primarily due to higher cumulative CO₂ emissions which dwarfed any potential impact of direct and indirect N₂O emissions on the overall GHG balance.

3.2. Effect of DM content and application technique

The amount of NH₃ emitted over the whole experiment was shown, after square root transformation, to be significantly reduced ($P < 0.0005$) with lower slurry DM content and with the trailing-shoe application compared to the splash-plate one (Table 4). However, when relating these losses to the quantity of N applied,

splash-plate plots applied with low dry-matter slurry showed significantly higher ($P < 0.0005$, square root transformed data) NH₃ losses than plots spread with an higher DM content.

In terms of direct N₂O emissions, a significant interaction was found between spreading technique and slurry DM content ($P < 0.005$). Generally, those fluxes were reduced at lower slurry DM content (Table 4). However, this reduction of direct N₂O emissions was no longer significant when expressing cumulative emissions of N₂O per unit of N applied.

The slurry application technique significantly affected both direct ($P < 0.05$, Box–Cox transformed data with $\lambda = -0.472$) and indirect N₂O emissions ($P < 0.0005$ on square root transformed data). On the other hand, the total amount of N₂O estimated to be emitted from the experimental plots over the course of the experiment, calculated as the sum of direct N₂O emissions measured on-site and indirect N₂O emissions derived from NH₃ volatilisation data (as defined in Section 2.4.3), was not affected by the application technique. However, the proportion of indirect N₂O in these emissions was reduced from about 45% for conventional broadcast application to 31% when using trailing-shoe.

Soil CO₂ efflux was also affected by a reduction in slurry DM content ($P < 0.01$), but the reduction of CO₂ emissions with a lower slurry DM content was only significant for plots spread with maize-derived slurry. Once expressed per unit of N applied, this effect no longer existed (Fig. 4). The change of application technique did not have any significant effect.

The amount of GHG emitted from slurry spread plots was dominated by CO₂ emissions, which dwarfed any potential effect of treatments on other gases, and therefore followed the same patterns as the one observed for soil CO₂ efflux (Fig. 4). As a consequence, GHG emissions from the soil were significantly affected by a reduction of slurry DM content ($P < 0.01$), but this effect no longer existed when those GHG emissions were expressed per unit of N applied.

Cumulative GHG emissions from trailing-shoe were, on average, 44% higher than those recorded for the same slurry when it was splash-plate applied, even though this difference was not significant due to a high variability of measured values.

3.3. Effect of timing of application

Cumulative fluxes for the three weeks following each application were compared, after logarithmic transformation of absolute values, using a Repeated measures ANOVA. Results showed a significant effect Timing * Fertiliser type (id. Control, CAN or slurry) on N₂O ($P < 0.0005$), NH₃ ($P < 0.005$), CO₂ ($P < 0.0005$) and total GHG emissions ($P < 0.0001$). NH₃ volatilisation from slurry spread plots was considerably higher when applying in July than for any other application (Fig. 5). Conversely, direct N₂O emissions were the lowest in July, whereas they were the highest in August. Overall, total gaseous N were the lowest when applying in April, with a 43% reduction compared to July.

Concerning plots fertilised with CAN, NH₃ volatilisation losses were not significantly different from control plots for any of the application dates with the exception of April (Fig. 5) and were always considerably lower than for slurry treatments. N₂O release from these plots was significantly higher in July than for the other months.

When subtracting background fluxes to treatment plots and expressing resulting fluxes per unit of N applied, the effect Timing * Fertiliser type could still be observed on direct ($P < 0.0001$, log transformed data) and indirect ($P < 0.05$, square root transformed data) N₂O fluxes. These effects were similar to those observed for absolute fluxes (data not shown). However, timing of application had a significant effect on total N₂O emissions ($P < 0.005$, log transformed data) only for slurry treatments.

Friedmann tests performed on CO₂, CH₄ and total GHG confirmed ($P < 0.0001$) the effect of application timing already observed in Fig. 5. The timing of fertiliser application had an effect on CH₄ ($P < 0.0001$, Friedman test), but the effect of such emissions of the total GHG budget was usually negligible.

In terms of total amount of GHG emitted for each three-week period, soil CO₂ efflux dwarfed the other emissions in terms of scale. These CO₂ emissions accounted for about 70% of total GHG emissions from CAN plots, and for up to 88% of those calculated for plots fertilised with slurry. For all treatments, there was a two to four fold increase in July relative to the other spreading dates. Total GHG emissions ranged from 0.2 to 1.6 t C ha⁻¹, to be compared with the 1–3 t C ha⁻¹ which had been applied.

While some plots did, indeed, appear to retain some of the applied C, some were shown to release more C than had been applied. A non-parametric Friedman test was carried out on the amount of CO₂ emitted from slurry treatments (corrected by controls and expressed in % of C applied). There was a significant effect of the

Table 4

Cumulative gaseous fluxes for each slurry treatment (in kg CO₂-eq ha⁻¹), integrated from field measurements over the entire experiment (428 days). Fluxes are expressed as mean values \pm standard errors. Significant differences between treatments are given by the letters beside each value (result from a Fisher LSD test, $P < 0.05$).

Treatment	N ₂ O indirect	N ₂ O direct	CO ₂ ($\times 10^3$)	CH ₄
Control	26 \pm 8 ^a	185 \pm 41 ^e	21.4 \pm 0.6 ^b	97 \pm 10 ^k
SP.G.H	514 \pm 39 ^b	657 \pm 16 ^f	29.1 \pm 0.3 ^j	199 \pm 27 ^l
SP.G.L	369 \pm 21 ^c	449 \pm 70 ^g	26.4 \pm 0.9 ⁱ	97 \pm 24 ^k
SP.M.H	494 \pm 11 ^b	640 \pm 38 ^f	32.3 \pm 2.3 ^j	129 \pm 38 ^{kl}
SP.M.L	371 \pm 14 ^c	437 \pm 65 ^g	23.2 \pm 0.6 ^{hi}	68 \pm 24 ^k
TS.M.L	279 \pm 11 ^d	575 \pm 32 ^f	29.1 \pm 0.4 ^{ij}	202 \pm 62 ^l

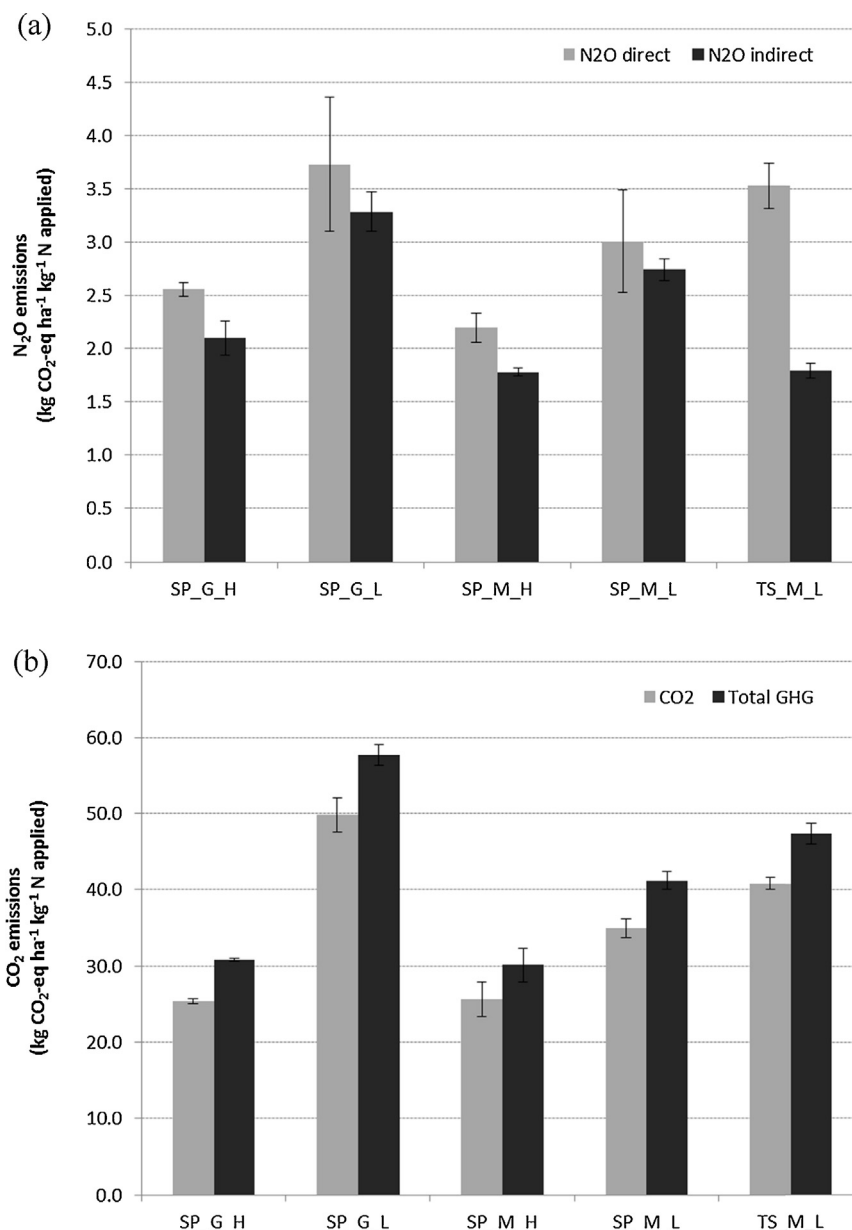


Fig. 4. Mean cumulative (a) direct and indirect N₂O, and (b) CO₂ and total GHG emissions fluxes for each slurry treatment, integrated from field measurements over the entire experiment (428 days) and corrected by controls. For each graph, standard errors are given as error bars.

application date ($P < 0.0001$), with some plots emitting an extra amount of CO₂ (compared to control plots) equal to up to 286% of the applied slurry C.

4. Discussion

4.1. Limitations of methods

In order to measure CO₂, CH₄ and N₂O emissions, chambers were placed at the soil surface, something which often modifies the gas flux by changing the vertical profile of the gas concentration, the energy balance and the turbulent regime (Rochette, 2011).

In this experiment, chamber walls were inserted about 0.02 m into the soil, to limit lateral gas exchange (Healy et al., 1996). However, subsequent soil disturbances may affect the measured rate of gas exchanges between the soil and the atmosphere (Matthias et al., 1980). As a consequence, Rochette (2011) suggest the use of collars that are inserted into the ground prior to the chamber

deployment. However, collars may also affect soil conditions, by preventing run-off and shading the soil, and gas exchanges, by formation of shrinkage cracks at the collar–soil interface (Rochette, 2011). In the present experiment, chambers were directly pushed into the ground, with no collar insertion prior to their deployment. Indeed, the presence of collars prior to the application of treatments would not have permitted a homogeneous slurry application pattern within the plots. Furthermore, the small size of the measuring chambers, relative to the size of the plots, led us to consider each measurement as an isolated sampling point within the plot. Thus, varying the location of the chamber within each plot, from one sampling day to the other, allowed us to integrate more spatial variability in trace gas fluxes.

The driving factors of such fluxes are usually no longer constant during the gas sampling time, and therefore no linear increase or decrease of the gas concentration inside the chamber, over time, is expected. Nevertheless, the use of a linear regression for

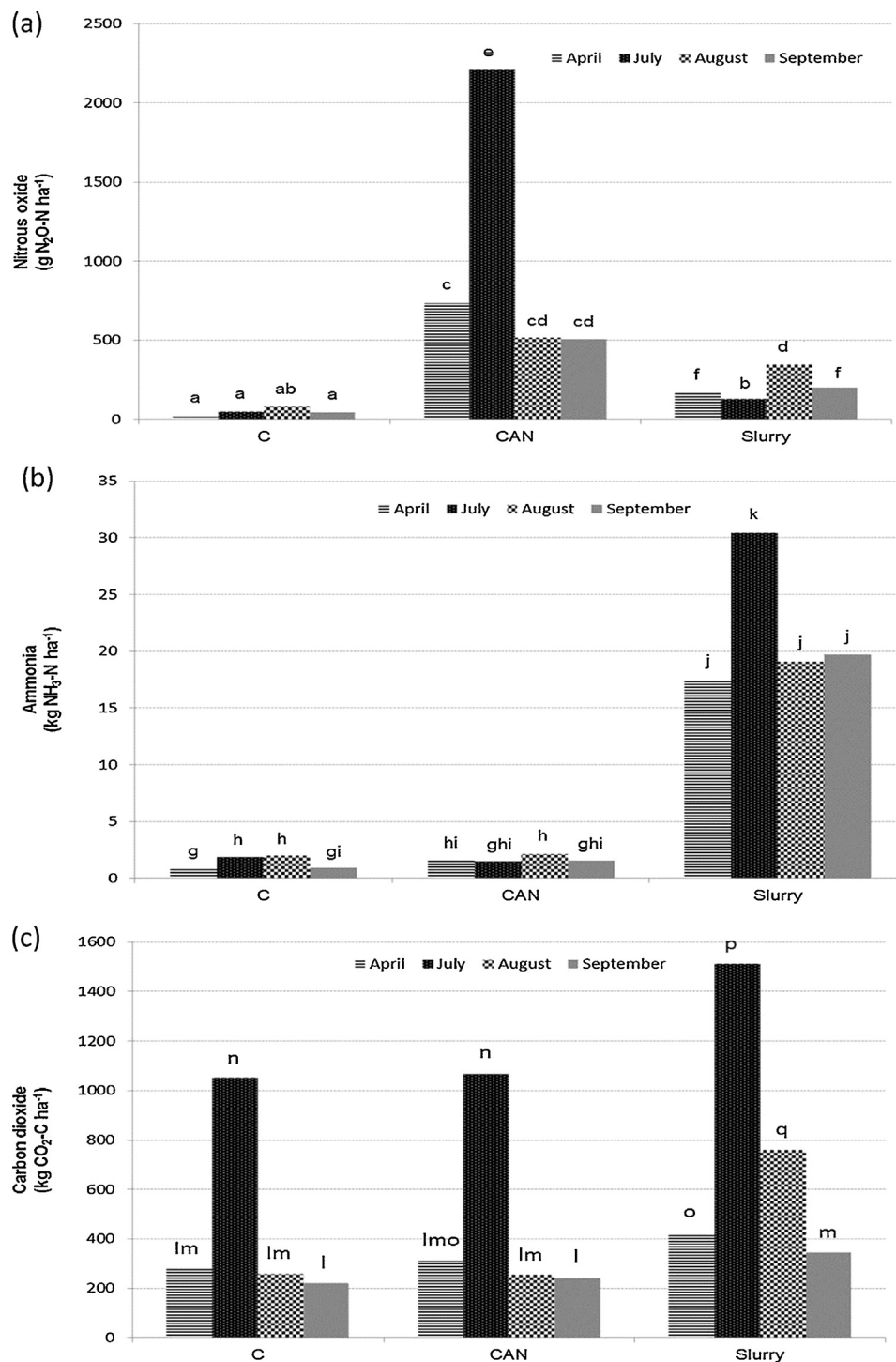


Fig. 5. Cumulative fluxes of (a) nitrous oxide, (b) ammonia, and (c) carbon dioxide from experimental plots over the first three weeks following the application of fertiliser. The four application dates were 24 April, 20 July, 17 August, and 20 September 2009. Significant differences between treatments are given by the letters beside each value (result from a Fisher LSD test, $P < 0.05$).

calculating CO_2 fluxes has been supported by keeping the closure time short and assuming the concentration change over time to be linear (Kutzbach et al., 2007).

In terms of N_2O emissions, even though there is an increasing body of evidences that, under certain conditions, the use of a linear approach to calculate N_2O flux rates from closed chamber measurements may be inappropriate (Healy et al., 1996; Rochette, 2011), the decision to use a linear regression model, in the present experiment, was supported by the fact that linearity tests conducted both

in the field and in controlled conditions (data not shown) showed that measured N_2O concentrations were (for controls and slurry treatments at least) within the linear range of the N_2O accumulation curve inside the chamber over time. However, the very high N_2O fluxes derived from CAN-fertilised plots (see Section 3) may have been underestimated.

The use of a 2-h measurement window was validated against ALFAM outputs. Previous ammonia emissions measurements (Meade et al., 2011) had found good agreement between integrated

horizontal flux measurements and ALFAM outputs. Therefore, there was confidence that this would be a robust comparison. Good agreement was observed between measurements and ALFAM outputs. This is due to the fact that 50% of emissions occur during the first 6 h post-application of slurry and most of this period was covered by measurements.

4.2. Comparison between mineral fertiliser and cattle slurry over the entire experiment

Ammonia losses from CAN fertilised plots were quite low, compared to slurry treatments, averaging 2.9% of the applied N. The ratios calculated during this experiment are similar to the values of 1–2.5% reported in the literature for non-calcareous soils (van der Weerden and Jarvis, 1997). The amount of NH_3 volatilised after applying slurry, on the other hand, accounted for 30.3–70.8% of applied total N. Similarly, Misselbrook et al. (2000) found NH_3 losses equal to 1.5% of total N after application of NH_4NO_3 compared to 59% with cattle slurry.

By contrast, plots amended with slurry displayed much lower N_2O emissions than those fertilised with CAN. Indeed, a great proportion of slurry-derived N was probably lost in the atmosphere, through the NH_3 volatilisation process, before even penetrating the upper soil layers, which subsequently would have decreased the soil N pool available to both nitrifying and denitrifying microorganisms.

Cumulative N_2O and NH_3 data fully support the idea of a possible trade-off between both fertiliser types. The additional $\text{NH}_4\text{-N}$, saved from volatilisation when applying CAN, is nitrified and denitrified by soil microbial communities, leading to additional N_2O losses compared to organic fertilisers applied onto grassland soils. These decreased N_2O emission factors associated with slurry application possibly arise from the fact that urea in freshly prepared slurry, as used in this experiment in contrast to the stored slurry applied in normal agricultural practice, must be ammonified prior to nitrification and denitrification, allowing more time for plant uptake. Slurry also contain much organic N which will not be immediately mineralised and will only be gradually available for NH_3 volatilisation, nitrification and denitrification processes, which offers an explanation for the lower N_2O emission peaks observed for slurry treatments (Lockyer and Whitehead, 1990).

However, comparisons between studies are difficult because the behaviour of different fertilisers depends on soil and crop type as well as environmental conditions. Velthof and Mosquera, (2011) observed higher emissions of N_2O from soils fertilised with CAN than from soils spread with cattle slurry, while Ball et al. (2004) found lower emissions from organic N additions compared to inorganic fertiliser application. Jones et al. (2007) reported higher N_2O emissions after application of NH_4NO_3 than after spreading cattle slurry in the first year of their experiment (emission factors of 1.4% and 0.5%, respectively), but no significant difference in the second year. Other studies reported increased N_2O losses when applying ammonium- or urea-based fertilisers (Ellis et al., 1998; Jin et al., 2010) while Sistani et al. (2010) found no significant differences, in terms of N_2O emissions, between surface-applied swine effluent and urea treatments applied to no-till maize (*Zea mays* L.).

The emission factors for N_2O of 1.6% and 0.8% observed in this study with CAN and cattle slurry additions, respectively, are in the range of those reported elsewhere in the literature (Jones et al., 2007; Velthof and Mosquera, 2011). This supports the use of different emission factors for organic and mineral fertilisers in GHG inventories rather than assuming a default of 1% of N applied being emitted as N_2O regardless of the N source (IPCC, 2006).

The input of readily available C from manures and slurries has been shown to enhance CO_2 release from soils during the first few days after application (e.g. Rochette et al., 2006) but after the

slurry-derived soluble C pool is exhausted, soil respiration rates usually return to background levels. In this experiment, there was an increase in soil CO_2 efflux following slurry application. However, the additional C mineralisation from slurry spread plots (compared to controls) remained significant for several weeks and reached $60 \pm 7\%$ of total C applied at the end of the experiment. This observation could be due to the use of formulated mixture of urine and faeces to get the low and high DM (mostly having low C:N ratios) which was easily mineralisable to provide the carbon substrate needed for CO_2 efflux. In addition to this the urine and faeces mixtures were freshly prepared which contained labile carbon that can be easily available for soil microbes for its respiration resulting in CO_2 efflux.

It is important to mention that the increase in soil respiration when adding readily available and metabolisable C to the system can be partly offset by an increase in photosynthesis (Soussana et al., 2004), and therefore an increase of gross primary production (GPP), from the grass cover which would further reduce the difference between both types of fertiliser in terms of full field-scale GHG budget. Soussana et al. (2004) showed that moderately enhanced N fertilisation increases the organic matter input to the soil proportionally more than it increases the process of C mineralisation, whereas intensive fertilisation stimulates mineralisation and therefore, enhances C losses. Furthermore, it has been shown that the addition of organic manures to grassland plots is more likely to increase C storage in soils, compared to inorganic fertilisers, but also increases rates of soil respiration, leading to a possible net CO_2 loss of $4.9 \text{ g CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ on cattle slurry treatment (Jones et al., 2006).

Manure organic matter (OM) is also a key driver of N transformations and losses. It can be used by soil micro-organisms, such as heterotrophic nitrifiers and denitrifiers, both as a structural element and, mainly, as an energy source (Granli and Bockman, 1994). Therefore, it is clear that the fate of slurry OM and N are closely linked and that GHG mitigation strategies need to consider both C and N dynamics concurrently in soil and crops (Petersen and Sommer, 2011).

4.3. Effect of DM content and application technique

The reduced emission of NH_3 observed when applying slurry at the lower slurry DM content is consistent with the results from slurry dilution experiments (Sommer and Olesen, 1991; Mkhabela et al., 2009). However, when relating these losses to the quantity of N applied, NH_3 volatilisation (as % total N applied) increased with diluted slurry. This contradicts the observations of Mkhabela et al. (2009) who found a general trend towards lower NH_3 losses (in % $\text{NH}_4\text{-N}$ applied) from diluted hog slurry. Smith et al. (2000) also found a reduction of NH_3 losses (in % $\text{NH}_4\text{-N}$ applied) from diluted slurry when using splash-plate and band-spread techniques, but not when using trailing-shoe or shallow injection methods.

The trailing-shoe technique is usually recommended as an efficient NH_3 abatement technique when applying slurry to grassland soils (Misselbrook et al., 2002). In this study the trailing-shoe application reduced NH_3 losses by 24% compared to the splash plate one, which is less than the 40–60% reduction found in previous studies (e.g. Smith et al., 2000; Misselbrook et al., 2002).

The work presented in this paper support the idea of a possible trade off between NH_3 and N_2O , even though the increase of direct N_2O when using trailing-shoe was not significant. Only a few studies have compared N_2O emissions from low trajectory slurry applications, such as the trailing-shoe technique, with the traditional broadcast application. Wulf et al. (2002) did not observe any significant differences between splash-plate and trailing-shoe application in terms of direct N_2O emissions. However, as they observed lower NH_3 losses following trailing-shoe application of

slurry, this reduced the calculated amount of indirect N_2O emissions. Consequently, they considered trailing-shoe to be the most effective way to reduce non- CO_2 GHG emissions (in CO_2 -eq) from grassland soils. In the experiment presented here, the calculated total amount of N_2O emitted from slurry spread plots was not affected by the application technique, but the proportion of indirect N_2O (as defined in Section 2.4.3) in these emissions were reduced from about 45% for conventional broadcast application to 31% when using trailing-shoe. In terms of strategies to mitigate GHG emissions from grassland soils, it is therefore essential to increase the number of studies assessing the effect of trailing-shoe on such emissions as it is considered to be the most effective alternative to splash-plate application in many grassland areas (Smith et al., 2000; Lalor and Schulte, 2008) and tend to offer more flexibility in terms of available spreading days (Lalor and Schulte, 2008).

Methane emissions from the various treatments were generally lower than other GHG emissions. CH_4 uptake episodes were even recorded on a few occasions (data not shown), mainly in control plots and a few weeks after treatment application on fertilised plots. Soil mediated CH_4 oxidation provides an important sink for both atmospheric CH_4 and for CH_4 produced in situ (Amaral et al., 1998). However, agricultural practices can have adverse impacts on the CH_4 oxidising ability of soils (as reviewed by Hütsch, 2001). Several studies have demonstrated that elevated soil N, particularly in the form of NH_4^+ , may significantly reduce CH_4 oxidation rates (Steudler et al., 1989; Bodelier and Laanbroek, 2004). It has been suggested that the NH_4^+ may act as a competitive inhibitor of CH_4 for methane mono-oxygenase (MMO), the enzyme catalysing CH_4 oxidation (Bédard and Knowles, 1989). However a study by Reay and Nedwell (2004) on forest soils shows that it is NO_3^- rather than NH_4^+ which plays a powerful inhibitory effect on CH_4 oxidation capacity. Further work is needed to elucidate the mechanisms in order to explain this contradictory observation.

Nitrogen fertilisation is one key factor inhibiting CH_4 oxidation in agricultural soils. In his review on CH_4 oxidation in non-flooded agricultural soils, Hütsch (2001) report that, immediately after application of NH_4^+ -N based fertiliser, CH_4 oxidation in soils may be strongly inhibited by NH_4^+ , which would explain, in the present study, why the highest CH_4 emissions were observed in the first week after treatment application and why CH_4 uptake was observed preferentially on non-fertilised plots and only a few weeks after fertilisation on CAN- or slurry-applied plots.

Animal slurries can cause CH_4 emissions immediately after application to soil (Sommer et al., 1996; Chadwick and Pain, 1997; Wulf et al., 2002). These authors concluded that such emissions may result from the volatilisation of CH_4 dissolved in the slurry or from the microbial degradation of slurry-derived compounds rather than from the soil itself. There was significant increase ($P < 0.05$) in CH_4 release from amended plots applied with trailing-shoe (Table 5), but, as discussed before; these emissions had a marginal impact on the total amount of GHG emitted from each plot. The higher CH_4 release from trailing-shoe applied soils, compared to those where slurry was applied using the conventional broadcast method, could be partly explained by higher amount of NH_4^+ -N preserved from volatilisation losses and, hence, penetrating the soil, where it acted as an inhibitor for CH_4 oxidation, as stated in the previous paragraph. The trailing-shoe application pattern may also create, under wet conditions, anaerobic sites where CH_4 might be produced by methanogenic bacteria (Wulf et al., 2002).

4.4. Effect of timing of application

NH_3 volatilisation from slurry spread plots was considerably higher when applying in July than for any other application (Fig. 5). Conversely, direct N_2O emissions were the lowest in July, whereas they were the highest in August. Overall, total gaseous N were the

Table 5

Non-parametric Spearman rank correlation ($P < 0.05$) calculated between fluxes measured on the field and soil/weather parameters (whenever these were measured). Significant correlations were marked with a star (*).

Parameters tested	Spearman rank order correlation
(a) Nitrous oxide	
Mean air temperature during sampling period	0.061838*
Cumulative solar radiation during sampling period	−0.055577*
Rainfall (24 h before sampling)	0.232639*
Soil temperature	−0.167323*
WFPS	0.294180*
(b) Ecosystem respiration	
Mean air temperature during sampling period	0.373653*
Cumulative solar radiation during sampling period	0.211320*
Rainfall (24 h before sampling)	0.219953*
Soil temperature	0.688280*
WFPS	−0.375021*

lowest when applying in April, with a 43% reduction compared to July. In terms of farmers' perspectives, this is of great importance as such reduction of gaseous N losses occurs in a period where the N requirement of the herbage is the largest, optimising N fertilisation and reducing the need for a supplementation with mineral N (Carton and Magette, 1999). Therefore, this work provides field based evidence as initial indication that spring application is not only of environmental interest, but also brings agronomic benefits to the farmer. As there are large ranges in the conditions in any one-day within each season, it is necessary to stress that the field based evidence was observed in the conditions that was experienced at the time of the field experiment and some caution should be exercised not to extrapolate to other conditions and generalise the observations to most situations.

NH_3 volatilisation from land spread slurry mainly occurs in the first 24–48 h after application (Misselbrook et al., 2002) and the main environmental driving factors are air/soil temperature, wind speed as well as air humidity and solar radiation (Sommer et al., 2003). Therefore, the high volatilisation rates observed from slurry plots could be linked to the fact that slurry was applied on a warm and dry sunny day which favoured high evaporation rates and therefore NH_3 losses. In August, although air temperature was slightly higher than in July, lower solar radiation and higher air moisture reduced N volatilisation losses.

A possible variation in the pH of applied slurry (not measured in this experiment), from one application date to the other, could have also contributed to the variation in the rate of NH_3 volatilisation. Indeed, a higher pH would increase the ratio $\text{NH}_3:\text{NH}_4^+$ in the slurry (Sommer et al., 2003), thus potentially increasing NH_3 losses. In the present experiment, cow diet was controlled and remained the same throughout the season, thus minimising the variations in the composition of urine and faeces. It was therefore assumed that any slight variation of the pH of applied slurry was unlikely to have offset the effect of environmental factors on NH_3 volatilisation post-spreading.

N_2O losses are driven not only by N inputs, but also by climatic and soil parameters such as soil texture, temperature and WFPS as well as plant N demand (Smith et al., 2003). WFPS is directly dependent on both precipitation and the clay content of soil (which influence the water holding capacity) and this has been observed to be the primary driver for the seasonality of N_2O emissions (Dobbie and Smith, 2003). In the present study, whenever soil parameters could be measured, fluxes were shown to be mainly and positively correlated with soil WFPS and rainfall data (Table 5)

Table 6

Direct, indirect and total N₂O emissions measured over the three weeks following each application (in kg CO₂-eq ha⁻¹ kg⁻¹ N applied). Results from a Fisher LSD test ($P < 0.05$) are given by the letters beside each flux.

	Direct N ₂ O	Indirect N ₂ O	Total N ₂ O
(a) Calcium ammonium nitrate			
April	2.41 (±0.90) ^a	0.12 (±0.02) ^f	2.54 (±0.88) ^j
July	7.26 (±5.15) ^b	0.12 (±0.04) ^f	7.38 (±5.19) ^{jk}
August	1.69 (±0.12) ^a	0.17 (±0.05) ^f	1.86 (±0.13) ^{jk}
September	1.66 (±0.07) ^{ac}	0.12 (±0.04) ^f	1.78 (±0.09) ^{jk}
(b) Slurry			
April	0.73 (±0.06) ^d	1.84 (±0.16) ^g	2.56 (±0.19) ^k
July	0.61 (±0.10) ^e	3.23 (±0.19) ^h	3.84 (±0.24) ^l
August	1.60 (±0.14) ^a	2.20 (±0.18) ⁱ	3.79 (±0.22) ^l
September	0.96 (±0.07) ^{cd}	2.29 (±0.14) ⁱ	3.25 (±0.17) ^m

which would explain the high emission rates observed after the third application, in August 2009. In addition, grass N response in terms of N uptake was shown to be reduced in autumn compared to spring, with 10.3 kg DM yield kg⁻¹ N applied in September compared to the 15.1 kg DM yield kg⁻¹ N applied measured in March/April (O'Donovan et al., 2004). Direct emissions in spring and autumn were reduced compared to those measured in July due to lower temperatures and rainfall (see Table 6).

In terms of total amount of GHG emitted for each three-week period, soil CO₂ efflux dwarfed the other emissions in terms of scale. These CO₂ emissions accounted for about 70% of total GHG emissions from CAN plots, and for up to 88% of those calculated for plots fertilised with slurry. For all treatments, there was a two to four fold increase in July relative to the other spreading dates. Higher summer emissions were to be expected as soil respiration exhibits an exponential response to increases in soil temperature (Lloyd and Taylor, 1994). In addition, the CO₂ losses upon slurry application have to be considered in the context that 1–3 t C ha⁻¹ had been applied. As total emissions ranged from 0.2 to 1.6 t C ha⁻¹, there was undoubtedly the potential for additional C sequestration from the carbon within the applied slurry.

While some plots did, indeed, appear to retain some of the applied C, some were shown to release more C than had been applied. This suggests that an additional amount of soil derived C (in comparison with control plots) was mineralised when cattle slurry was applied at the soil surface. Such phenomenon, known under the generic term of “priming effect”, has been widely investigated and is defined, in studies of C turnover, as an extra decomposition of organic C after addition of easily decomposable organic substances to soil (Dalenberg and Jager, 1989).

Bol et al. (2014) developed a laboratory method to quantify the priming effect of applying cattle slurry onto grassland soil, and to follow the fate of slurry derived C into the soil. This method, based on the ¹³C natural abundance tracer technique, uses the natural difference in isotopic signature between C₃ (e.g. rye-grass) and C₄ (e.g. maize) vegetation. By comparing CO₂ effluxes from soils amended with either grass or maize-based slurry and after assuming that CO₂ emission rates from both slurry types are equivalent, it is possible to estimate the proportion of slurry-derived and soil-derived CO₂-C from the measured total CO₂ efflux. In most statistical analyses carried on in this study, there was no significant difference between both types of slurry, which may allow one step further in the investigation of the effect of land spread cattle slurry on soil C dynamics and the resulting CO₂ balance between the system (soil–grass) and the atmosphere.

However, there was no characterisation of the impact of slurry application on CO₂ via photosynthesis. With a potentially higher plant growth and a longer remaining growing season when applying slurry in spring, there may be higher C sequestration rates in plant biomass compared to plots amended in summer (Smith et al.,

2010; Soussana et al., 2004, 2007) which may counterbalance the differences in respiratory losses between treatments.

5. Conclusions

The results of this study show a clear difference between CAN-fertilised and cattle slurry-spread plots in terms of GHG emissions from soil. Most particularly, cumulative direct N₂O emissions, and corresponding emission factors, were shown to be significantly higher when applying synthetic fertiliser.

Emission factors from CAN-fertilised and cattle slurry plots were affected by soil and weather conditions, underlining the importance of timing of application on N₂O emissions. The use of a single EF value for national GHG inventories, independent from the fertiliser type, the soil conditions and the climate, is not optimal for an accurate assessment of direct N₂O emissions from the grassland.

The trailing-shoe is widely considered to be the most effective alternative to conventional splash-plate application to grassland. However, in terms of GHG balance, the potential decrease in indirect N₂O emissions, calculated from a reduction of NH₃ volatilisation losses, could be easily offset by an increase in direct N₂O emissions and ecosystem respiration.

Switching from summer to spring application is much more efficient for mitigation of both NH₃ and GHG as all gaseous emissions from the soil were reduced, due to favourable soil and climatic factors. Furthermore, the potential for a trade-off between NH₃ and N₂O emissions was cancelled, leading to an overall positive effect on reactive N losses and offering agronomic benefits to farmers.

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References

- Amaral, J., Ren, T., Knowles, R., 1998. Atmospheric methane consumption by forest soils and extracted bacteria at different pH values. *Appl. Environ. Microbiol.* 64, 2397–2402.
- Ball, B.C., McTaggart, I.P., Scott, A., 2004. Mitigation of greenhouse gas emissions from soil under silage production by use of organic manures or slow-release fertilizer. *Soil Use Manage.* 20, 287–295.
- Bédard, C., Knowles, R., 1989. Physiology, biochemistry, and specific inhibitors of CH₄, NH₄⁺, and CO oxidation by methanotrophs and nitrifiers. *Microbiol. Rev.* 53, 68–84.
- Bodelier, P.L.E., Laanbroek, H.J., 2004. Nitrogen as a regulatory factor of methane oxidation in soils and sediments. *FEMS Microbiol. Ecol.* 47, 265–277.
- Bol, R., Moering, J., Kuzyakov, Y., Amelung, W., 2014. Quantification of priming and CO₂ respiration sources following slurry-C incorporation into two grassland soils with different C content. *Rapid Commun. Mass Spectrom.* 17, 2585–2590.
- Brink, C., Kroeze, C., Klimont, Z., 2001. Ammonia abatement and its impact on emissions of nitrous oxide and methane in Europe: Part 1. Method. *Atmos. Environ.* 35, 6299–6312.
- Carton, O.T., Magette, W.L., 1999. *Land Spreading of Animal Manures, Farm Wastes and Non-Agricultural Organic Wastes: Part 1. Manure (and Other Organic Wastes) Management, Guidelines for Intensive Agricultural Enterprises. Project 4026.* Teagasc, Dublin, Ireland.
- Chadwick, D.R., Pain, B.F., 1997. Methane fluxes following slurry applications to grassland soils: laboratory experiments. *Agric. Ecosyst. Environ.* 63, 51–60.
- Chadwick, D.R., Pain, B.F., Brookman, S.K.E., 2000. Nitrous oxide and methane emissions following application of animal manures to grassland. *J. Environ. Qual.* 29, 277–287.
- Dalenberg, J.W., Jager, G., 1989. Priming effect of some organic additions to C-14-labeled soil. *Soil Biol. Biochem.* 21, 443–448.
- Dendooven, L., Bonhomme, E., Merckx, R., Vlassak, K., 1998. Injection of pig slurry and its effects on dynamics of nitrogen and carbon in a loamy soil under laboratory conditions. *Biol. Fertil. Soils* 27, 5–8.
- Department Of Agriculture Food and the Marine, 2013. *Annual Review and Outlook for Agriculture, Food and the Marine 2012/2013.* DAFM, Dublin 2, Ireland.
- Dobbie, K.E., Smith, K.A., 2003. Nitrous oxide emission factors for agricultural soils in Great Britain: the impact of soil water-filled pore space and other controlling variables. *Global Change Biol.* 9, 204–218.

- Donovan, W.C., Logan, T.J., 1983. Factors affecting ammonia volatilization from sewage-sludge applied to soil in a laboratory study. *J. Environ. Qual.* 12, 584–590.
- Dosch, P., Gutser, R., 1996. Reducing N losses (NH_3 , N_2O , N_2) and immobilization from slurry through optimized application techniques. *Fert. Res.* 43, 165–171.
- Duffy, P., Hanley, E., Hyde, B.P., O'Brien, P., Ponzi, J., Cotter, E., Black, K., 2013. Ireland: Inventory Report 2013. EPA, Wexford, Ireland.
- Ellis, S., Yamulki, S., Dixon, E., Harrison, R., Jarvis, S.C., 1998. Denitrification and N_2O emissions from a UK pasture soil following the early spring application of cattle slurry and mineral fertiliser. *Plant Soil* 202, 15–25.
- European Union (EU), 2001. Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on national emissions ceilings for certain atmospheric pollutants. *Off. J. Eur. Union L* 309, 22–30.
- European Union (EU), 2009. Decision No. 406/2009/EC of the European Parliament and of the Council of 23 April 2009 on the effort of Member States to reduce their greenhouse gas emissions to meet the Community's greenhouse gas emission reduction commitments up to 2020. *Off. J. Eur. Union L* 140, 136–148.
- Franzluebbers, A.J., Haney, R.L., Hons, F.M., Zuberer, D.A., 1999. Assessing biological soil quality with chloroform fumigation incubation: Why subtract a control? *Can. J. Soil Sci.* 79, 521–528.
- Granli, T., Bockman, O.C., 1994. Nitrous oxide from agriculture. *Norweg. J. Agric. Sci. Suppl.* 12, 128.
- Gregorich, E.G., Rochette, P., Vandenbygaart, A.J., Angers, D.A., 2005. Greenhouse gas contributions of agricultural soils and potential mitigation practices in Eastern Canada. *Soil Tillage Res.* 83, 53–72.
- Healy, R.W., Striegl, R.G., Russell, T.F., Hutchinson, G.L., Livingston, G.P., 1996. Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange: identification of physical processes. *Soil Sci. Soc. Am. J.* 60, 740–747.
- Humphreys, J., 2008. Nutrient issues on Irish farms and solutions to lower losses. *Int. J. Dairy Technol.* 61, 36–42.
- Hütsch, B.W., 2001. Methane oxidation in non-flooded soils as affected by crop production – invited paper. *Eur. J. Agron.* 14, 237–260.
- Hyde, B.P., Carton, O.T., 2005. Manure Management Facilities on Farms and Their Relevance to Efficient Nutrient Use. Publication No. 42 (Winter Scientific Meeting 2005), FAO, Ireland.
- Hyde, B.P., Carton, O.T., O'toole, P., Misselbrook, T.H., 2003. A new inventory of ammonia emissions from Irish agriculture. *Atmos. Environ.* 37, 55–62.
- IPCC, 2006. IPCC Guidelines for National Greenhouse Gas Inventories. Institute for Global Environmental Strategies (IGES), Tokyo.
- IPCC, 2007. Climate Change 2007, The Physical Science Basis – Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). Cambridge University Press, Cambridge.
- Jin, T., Shimizu, M., Marutani, S., Desyatkin, A.R., Izuka, N., Hata, H., Hatano, R., 2010. Effect of chemical fertilizer and manure application on N_2O emission from reed canary grassland in Hokkaido, Japan. *Soil Sci. Plant Nutr.* 56, 53–65.
- Jones, S.K., Rees, R.M., Kosmas, D., Ball, B.C., Skiba, U.M., 2006. Carbon sequestration in a temperate grassland; management and climatic controls. *Soil Use Manage.* 22, 132–142.
- Jones, S.K., Rees, R.M., Skiba, U.M., Ball, B.C., 2007. Influence of organic and mineral N fertiliser on N_2O fluxes from a temperate grassland. *Agric. Ecosyst. Environ.* 121, 74–83.
- Kutzbach, L., Schneider, J., Sachs, T., Giebel, M., Nykanen, H., Shurpali, N.J., Martikainen, P.J., Alm, J., Wilmking, M., 2007. CO_2 flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression. *Biogeosciences* 4, 1005–1025.
- Lalor, S.T.J., Schulte, R.P.O., 2008. Low-ammonia-emission application methods can increase the opportunity for application of cattle slurry to grassland in spring in Ireland. *Grass Forage Sci.* 63, 531–544.
- Leuning, R., Freney, J.R., Denmead, O.T., Simpson, J.R., 1985. A sampler for measuring atmospheric ammonia flux. *Atmos. Environ.* 19, 1117–1124.
- Lloyd, J., Taylor, J.A., 1994. On the temperature-dependence of soil respiration. *Funct. Ecol.* 8, 315–323.
- Lockyer, D.R., Whitehead, D.C., 1990. Volatilization of ammonia from cattle urine applied to grassland. *Soil Biol. Biochem.* 22, 1137–1142.
- Matthias, A.D., Blackmer, A.M., Bremner, J.M., 1980. A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *J. Environ. Qual.* 9, 251–256.
- Maynard, D.G., Kalra, Y.P., 1993. Nitrate and exchangeable ammonium nitrogen. In: Carter, M.R. (Ed.), *Soil Sampling and Methods of Analysis*, vol. 1. Lewis Publishers, Boca Raton.
- Meade, G., Pierce, K., O'Doherty, J.V., Mueller, C., Lanigan, G., McCabe, T., 2011. Ammonia and nitrous oxide emissions following land application of high and low nitrogen pig manures to winter wheat at three growth stages. *Agric. Ecosyst. Environ.* 140, 208–217.
- Misselbrook, T.H., Smith, K.A., Johnson, R.A., Pain, B.F., 2002. Slurry application techniques to reduce ammonia emissions: results of some UK field-scale experiments. *Biosyst. Eng.* 81, 313–321.
- Misselbrook, T.H., Van Der Weerden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J., Smith, K.A., Phillips, V.R., Demmers, T.G.M., 2000. Ammonia emission factors for UK agriculture. *Atmos. Environ.* 34, 871–880.
- Mkhabela, M.S., Gordon, R., Burton, D., Smith, E., Madani, A., 2009. The impact of management practices and meteorological conditions on ammonia and nitrous oxide emissions following application of hog slurry to forage grass in Nova Scotia. *Agric. Ecosyst. Environ.* 130, 41–49.
- O'Donovan, M., Delaby, L., Stakelum, G., Dillon, P., 2004. Effect of autumn/spring nitrogen application date and level on dry matter production and nitrogen efficiency in perennial ryegrass swards. *Irish J. Agric. Food Res.* 43, 31–41.
- Petersen, S.O., Sommer, S.G., 2011. Ammonia and nitrous oxide interactions: roles of manure organic matter management. *Anim. Feed Sci. Technol.* 166/167, 503–513.
- Reay, D.S., Nedwell, D.B., 2004. Methane oxidation in temperate soils: effects of inorganic N. *Soil Biol. Biochem.* 36, 2059–2065.
- Rochette, P., 2011. Towards a standard non-steady-state chamber methodology for measuring soil N_2O emissions. *Anim. Feed Sci. Technol.* 166, 141–146.
- Rochette, P., Angers, D.A., Chantigny, M.H., Gagnon, B., Bertrand, N., 2006. In situ mineralization of dairy cattle manures as determined using soil-surface carbon dioxide fluxes. *Soil Sci. Soc. Am. J.* 70, 744–752.
- Sistani, K.R., Warren, J.G., Lovanh, N., Higgins, S., Shearer, S., 2010. Greenhouse gas emissions from swine effluent applied to soil by different methods. *Soil Sci. Soc. Am. J.* 74, 429–435.
- Smith, K.A., Ball, T., Conen, F., Dobbie, K.E., Massheder, J., Rey, A., 2003. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.* 54, 779–791.
- Smith, K.A., Clayton, H., McTaggart, I.P., Thomson, P.E., Arah, J.R.M., Scott, A., 1995. The measurement of nitrous oxide emissions from soil by using chambers. *Philos. Trans. R. Soc. Lond. A* 351, 327–338.
- Smith, K.A., Jackson, D.R., Misselbrook, T.H., Pain, B.F., Johnson, R.A., 2000. Reduction of ammonia emission by slurry application techniques. *J. Agric. Eng. Res.* 77, 277–287.
- Smith, P., Lanigan, G., Kutsch, W.L., Buchmann, N., Eugster, W., Aubinet, M., Ceschia, E., Beziat, P., Yeluripati, J.B., Osborne, B., Moors, E.J., Brut, A., Wattenbach, M., Saunders, M., Jones, M., 2010. Measurements necessary for assessing the net ecosystem carbon budget of croplands. *Agric. Ecosyst. Environ.* 139, 302–315.
- Søgaard, H.T., Sommer, S.G., Hutchings, N.J., Huijmans, J.F.M., Bussink, D.W., Nicholson, F., 2002. Ammonia volatilization from field-applied slurry – the ALFAM model. *Atmos. Environ.* 36, 3309–3319.
- Sommer, S.G., Générmont, S., Cellier, P., Hutchings, N.J., Olesen, J.E., Morvan, T., 2003. Processes controlling ammonia emission from livestock slurry in the field. *Eur. J. Agron.* 19, 465–486.
- Sommer, S.G., Olesen, J.E., 1991. Effects of dry-matter content and temperature on ammonia loss from surface-applied cattle slurry. *J. Environ. Qual.* 20, 679–683.
- Sommer, S.G., Sherlock, R.R., Khan, R.Z., 1996. Nitrous oxide and methane from pig slurry amended soils. *Soil Biol. Biochem.* 28, 1541–1544.
- Soussana, J.F., Allard, V., Pilegaard, K., Ambus, P., Amman, C., Campbell, C., Ceschia, E., Clifton-Brown, J., Czobel, S., Domingues, R., Flechard, C., Fuhrer, J., Hensen, A., Horvath, L., Jones, M., Kasper, G., Martin, C., Nagy, Z., Neftel, A., Raschi, A., Baronti, S., Rees, R.M., Skiba, U., Stefani, P., Manca, G., Sutton, M., Tubaf, Z., Valentini, R., 2007. Full accounting of the greenhouse gas (CO_2 , N_2O , CH_4) budget of nine European grassland sites. *Agric. Ecosyst. Environ.* 121, 121–134.
- Soussana, J.F., Loiseau, P., Vuichard, N., Ceschia, E., Balesdent, J., Chevallier, T., Arrouays, D., 2004. Carbon cycling and sequestration opportunities in temperate grasslands. *Soil Use Manage.* 20, 219–230.
- Stedler, P.A., Bowden, R.D., Melillo, J.M., Aber, J.D., 1989. Influence of nitrogen fertilization on methane uptake in temperate forest soils. *Nature* 341, 314–316.
- Stevens, C.J., Quinton, J.N., 2009. Diffuse pollution swapping in arable agricultural systems. *Crit. Rev. Environ. Sci. Technol.* 39, 478–520.
- UNECE, 1999. Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution to Abate Acidification, Eutrophication and Ground Level Ozone. United Nations Economic Commissions for Europe (UNECE), Geneva.
- UNFCCC, 1997. Kyoto Protocol to the United Nations Framework Convention on Climate Change. United Nations Framework Convention on Climate Change (UNFCCC), Kyoto.
- van der Weerden, T.J., Jarvis, S.C., 1997. Ammonia emission factors for N fertilizers applied to two contrasting grassland soils. *Environ. Pollut.* 95, 205–211.
- VanderZaag, A.C., Jayasundara, S., Wagner-Riddle, C., 2011. Strategies to mitigate nitrous oxide emissions from land applied manure. *Anim. Feed Sci. Technol.* 166/167, 464–479.
- Velthof, G.L., Mosquera, J., 2011. The impact of slurry application technique on nitrous oxide emission from agricultural soils. *Agric. Ecosyst. Environ.* 140, 298–308.
- Weslien, P., Klemmedtsen, L., Svensson, L., Galle, B., Kasimir-Klemmedtsen, A., Gustafsson, A., 1998. Nitrogen losses following application of pig slurry to arable land. *Soil Use Manage.* 14, 200–208.
- Wulf, S., Maeting, M., Clemens, J., 2002. Application technique and slurry co-fermentation effects on ammonia, nitrous oxide, and methane emissions after spreading: II. Greenhouse gas emissions. *J. Environ. Qual.* 31, 1795–1801.