How do emission rates and emission factors for nitrous oxide and ammonia vary with manure type and time of application in a Scottish farmland?

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Abstract

The use of livestock manure as an organic fertiliser on agricultural land is an attractive alternative to synthetic fertiliser. The type of manure and the timing and method of application can however be crucial factors in reducing the extent of nitrogen lost from the system. This is important not only to enhance crop production, but in controlling gaseous emissions, including nitrous oxide (N_2O) and ammonia (NH_3). Emissions of N_2O and NH_3 were measured for 12 months from two experiments at an arable site in Scotland, to determine the effect of manure type and the timing (season) of application. Emission factors (EFs) were calculated for each manure applied in each season, and compared to IPCC standard EFs of 1% for N_2O and 20% for $NH_{3.}$ Cattle farmyard manure, broiler litter, layer manure, and cattle slurry by surface broadcast and trailing hose application were applied to one experiment in October 2012 (autumn applications) and one in April 2013 (spring applications). Experimental areas were sown with winter wheat (*Triticum aestivum*) and manures applied at typical rates. Crop yield was recorded to allow calculation of N_2O and NH_3 emission intensities. Mean annual N_2O emissions across all manure treatments were greater from autumn (2 kg N_2O-N ha^{-1}) than spring (0.35 kg N_2O-N ha^{-1}) applications, and in the spring experiment were significantly lower from cattle slurry than other treatments. Ammonia emissions were generally greater (though not significantly) from spring than autumn applications. Significantly greater NH_3 emissions were measured from layer manure than all other manures at both times of application. N_2O and NH_3 EFs were highly variable depending on the season of application and manure type. The mean autumn and spring N_2O EFs across all manure treatments were 1.72 % and -0.33 % respectively, and mean NH_3 EFs across all treatments were 8.2 % and 15.0 % from autumn and spring applications, respectively. These results demonstrate large deviation from the IPCC default values for N_2O

and NH_3 EFs, and the considerable effect that manure type and time of application have on N_2O and NH_3 emissions.

Keywords: Nitrous oxide, ammonia, livestock manure, agriculture, emission factors.

How do emission rates and emission factors for nitrous oxide and ammonia vary with manure type and time of application in a Scottish farmland?

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1. Introduction

Manures and slurries provide a significant nitrogen (N) input to agricultural land. In 2011 the total N excreted by livestock in the EU was 9.2 Tg which is only 15 % less than the N added by synthetic fertilisers (Velthof et al., 2015). The large quantity of nutrients present in manures mean that they are commonly applied to agricultural land to recycle N, phosphorus and potassium for plant growth (Defra, 2010). However, considerable amounts of the applied manure N will not be utilised by crops as a result of nitrification and denitrification, and the subsequent emissions of nitrous oxide (N_2O) (Chadwick et al., 2011), dinitrogen (N_2) (Cardenas et al., 2007), and ammonia (NH_3) (Misselbrook et al., 2005a). Leaching of nitrate (NO_3^-) into groundwater and surface waters leads to further N loss from the soil (Rodhe et al., 2006) and other environmental impacts including eutrophication and soil acidification.

Globally, agricultural soil is responsible for 65 % of N_2O emissions (Reay et al., 2012), a greenhouse gas (GHG) approximately 300 times more powerful than CO_2, that is also responsible for stratospheric ozone layer depletion (Stocker et al., 2013). In the UK it is estimated that 73 % of anthropogenic N_2O emissions and 92 % of NH_3 emissions are from agricultural sources, including direct emissions from soils, animal wastes and manure stores (Dore et al., 2008; Skiba et al., 2012). Indirect N_2O emissions also result from deposition of volatilised NH_3 and NO_3^- leaching and transport in aquatic and terrestrial environments.

The potential for N_2O and NH_3 emission after manure applications to agricultural soil is dependent on a combination of manure properties and environmental conditions. High temperatures, high wind speed and low rainfall immediately following manure application promote NH_3 emissions from manures containing a high amount of readily available N (Meisinger and Jokela, 2000; Misselbrook et al., 2005a), meaning that the timing of application can be critical if significant losses of N from the soil are to be avoided. Conversely, loss of N via N_2O emissions is higher when manure is applied in wet conditions as N_2O production via denitrification will occur before the crop is able to utilise the available N. Nitrate leaching will also occur if excess rainfall and drainage take place between manure application and crop N uptake (Defra, 2010; Shepherd and Newell Price, 2013). It is generally recommended therefore to apply manures when crops are actively growing and removing N from the soil (Granli and Bockman, 1994; Meisinger and Jokela, 2000; Defra, 2010).

In the UK, manure application in autumn and winter is restricted by Nitrate Vulnerable Zone (NVZ) regulations to decrease NO_3^- pollution of aquatic environments. Expansion of these measures to other areas could assist in decreasing indirect N_2O emissions from NO_3^- leaching and direct N_2O emissions from denitrification if application in wet conditions is avoided. The time of application should aim to provide a balance between the need to apply manure during the period of maximum crop N requirement, and the need to reduce seasonal climate effects on emissions (Meisinger and Jokela, 2000). Reducing losses of N from the soil is also beneficial for crop growth as more N is available for use by the growing crop (Rodhe et al., 2006; Shepherd, 2009).

The magnitude of N_2O and NH_3 emissions generated from manures is also dependent on their total-N content and the proportion present as readily available N (ammonium-N and uric acid-N), which varies with manure type (Defra, 2010; Shepherd and Newell-Price, 2013). Large quantities of readily available N (35 - 70 % of total N) are typically found in slurries and poultry manures, compared to only 10 - 25 % of total N in farmyard manure (FYM) (Defra, 2010). Manures containing large amounts of readily available N have a higher probability of losing N via NH_3 volatilization (Misselbrook et al., 2005a), N_2O production (Chadwick et al., 2011), or as a result of NO_3^- leaching (Chambers et al., 2000; Dampney et al., 2000; Shepherd, 2009). Manure moisture content can also affect N_2O emissions, as an increase in soil moisture can enhance the production of N_2O, with greatest N_2O emissions most likely to occur between 50 - 70 % WFPS (Flechard et al., 2007). Slurry typically has a moisture content of >90 %, increasing the risk of high N_2O emissions after application (Jorgensen et al., 1998). The moisture content of manures can also affect NH_3 emission rate, and slurries with higher moisture contents are generally associated with lower NH_3 emissions as they rapidly infiltrate into the soil, with the majority of the emission typically occurring in the 12 hours post-application (Sommer and Hutchings, 2001). Poultry litter, in contrast, has a much lower moisture content and a lower initial loss of NH_3, but emissions occur over a longer timescale as uric acid is broken down and urea hydrolysed to NH_4^+ (Meisinger and Jokela 2000; Jones et al., 2007). It has also been suggested that the C:N ratio of organic manures may affect N losses from soil. Akiyama et al. (2004) argue that higher C:N ratios in manure compared with inorganic chemical fertilisers provide optimum conditions for denitrification. The high C contents of organic manures (typically 35 % organic C), can also stimulate microbial activity, thereby creating anaerobic zones in the soil that allow denitrification and N_2O production to occur at a lower %WFPS than for chemical fertilisers (Akiyama et al., 2004). Incorporation of manures into the soil immediately after application, and the method of slurry application can also influence the extent of N_2O and NH_3 emissions (Webb et al., 2010). However, the use of these methods and their degree of success will depend on the presence/stage of crop growth.

The amount of N_2O or NH_3 emitted from N sources applied to soils is often calculated using an emission factor (EF), which defines the quantity of N_2O or NH_3 emitted as a proportion of the total N applied. The UK currently uses the IPCC's Tier 1 EF in its national N_2O inventory, where N_2O emissions from soils receiving organic amendments are equal to 1 % of the total N applied (IPCC, 2006), with no accounting for locally variable factors such as soil type or climate, variations in manure type, or the time of application. The IPCC default EF for NH_3 emission following manure application to land is 20 % of the applied N. However, the EF used to estimate NH_3 emissions from manure application in the UK NH_3 emissions inventory is derived from an empirical model taking account of manure type and some soil and climatic factors (Nicholson et al., 2013).

The variety of conditions affecting N loss from soils amended with livestock manures mean it is imperative that applications are carefully managed to avoid significant environmental pollution. It is vital to understand how the form and time of application may affect environmental impacts. The results of the research presented in this paper which forms part of a nationwide project, will contribute to reducing uncertainty in the UK's agricultural GHG inventory, and will enhance the sustainability and GHG mitigation potential of farming systems (GHG, 2013). This study aimed to compare soil N_2O and NH_3 emissions and EFs following autumn and spring manure applications to arable land in Scotland. Nitrous oxide and NH_3 emissions were measured for all manure types following application in both seasons, and the suitability of the IPCC Tier 1 EFs to represent N_2O and NH_3 emissions from different manure types and seasons of application was assessed. Effects of the timing and form of manure application on crop yield and crop N uptake were also investigated, to assess the impact of the type and time of manure application on crop production.

2. Materials and Methods

2.1. Site description and experimental design

Two 12 month field experiments were undertaken at Boghall farm (NT 248653, 190 m elevation), in East-central Scotland in 2012/2013. Both experiments were located in the same field, on a sandy loam soil (pH 6, 6% OM), with a 30 year (1980-2009) site mean annual precipitation of 979 mm and mean daily temperature in July and January of 14.3 ^{o}C and 3.3 ^{o}C, respectively. Spring barley (*Hordeum vulgare*) had been grown in the field for the previous four years. The site was one of a network of UK sites measuring emissions as part of the UK GHG research platform, and was selected following a geographical assessment of UK arable land under a range of soil/climatic zones, and a 'gap analysis' to identify zones lacking in current/planned experimental data. The entire field, covering both experimental areas was sown with winter wheat (*Triticum aestivum*), a typical crop for the area, on 25th October 2012 at a seed rate of 400 m^{-2}. In the first experiment manures were applied on 3rd October 2012 to assess N_2O and NH_3 emissions following autumn applications. In the second experiment the crop was left untreated until 10th April 2013, when manures were applied to assess emissions from spring applications. The crop was harvested from both experimental areas on 15th September 2013, with all stubble left in the field and no new crop planted until after the experiment ended. Both experiments ran for a total of 12 months following the date of manure application.

Manure treatments (cattle farmyard manure (autumn only), CFYM; broiler litter, BL; layer manure, LM; cattle slurry by trailing hose application, CSTH; cattle slurry by surface broadcast application, CSSB) and a control (to which no manure was added) were applied to a fully replicated randomized block design with three blocks, in each experiment respectively.

Treatment plots were orientated in a NNE direction and measured 12 m x 6 m. Manures were applied at rates commonly practiced for the specific manure type, with target application rates for the solid manures of 180 kg total N ha^{-1}, and for slurry of 40 m^3 ha^{-1}. In the autumn experiment all manures apart from CFYM were incorporated into the bare soil 24 hours after application, and in the spring experiment they were top dressed on the growing crop. The plots were orientated at 20 degrees to the vertical, and 90 degrees to the prevailing wind to minimise the carry-over of volatilised NH_3 from one plot to another when making NH_3 emission measurements using wind tunnels. Target N application rates and the results of manure chemical analysis were used to calculate total manure application rates. Actual N application rates varied between treatments (Table 1) as a result of changes in the N concentration of the manures between analysis and application, and also due to the rate of manure that would be typically applied in practice for the respective manure types. All manures were sourced from local commercial farms in the autumn, and the un-used quantities were covered to prevent nutrient loss, and stored over-winter on site to enable use of the same materials in the spring experiments, allowing direct comparisons to be made. The slurry was mixed before application and applied in rows at 30 cm spacing using watering cans to simulate trailing hose application. To simulate surface broadcast application the slurry was divided into buckets and splashed evenly across the plots. Solid manures were applied evenly across the plots by hand. Details of treatments are displayed in Table 1. Throughout the experiments plant protection products were applied to meet crop growth requirements, with phosphorus and potassium fertilisers also applied to the plots seven days after spring manure applications.

2.2. N_2O and NH_3 emission measurements

Nitrous oxide emission measurements were made using the static chamber method, consistent with the Global Research Alliance guidelines (de Kleine and Harvey, 2012). At the start of each experimental period five square chambers (stackable) made of opaque polypropylene (400 mm x 400 mm x 400 mm, soil surface area coverage of 0.16 m^2) were inserted 5cm into the soil on each plot. The chambers remained *in situ* for the entire experiment but were removed when agricultural operations were taking place. Over the course of crop growth, chamber heights were extended using additional stackable chambers to enable sampling to continue. All chambers were stacked at the same time to maintain consistency in the experimental procedure, and the extensions remained in place throughout the growing season. Measurements were made for 12 months for each experiment to determine annual EFs, in compliance with IPCC guidelines. If emission measurements were short of the complete 365 day annual period the flux was extrapolated to 365 days to enable a direct comparison between autumn and spring experiments. Daily gas samples were taken on ten occasions over the first two weeks after manure application, with sampling frequency then reduced to two days a week for the following three weeks. A fortnightly sampling strategy was implemented for the next five months, and reduced to monthly sampling for the remaining six months. The closed static chamber technique described in Chadwick et al. (2014) was used to sample N_2O emissions, with sampling events undertaken between 10 am and 12 noon. On each sampling occasion lids were placed on the chambers and sealed for 40 minutes. After the 40 minute closure period 50ml gas samples were extracted from the chamber lids using a syringe through a valve with a 3-way tap, and transferred to pre-evacuated 20ml glass vials. Ten ambient air samples were taken to represent the concentration of N_2O in the chambers at time zero, and N_2O accumulation within the chambers was assumed to be linear over the 40 minute closure period following a detailed assessment in Chadwick et al. (2014). Following transportation back to the laboratory the N_2O concentration of the gas samples was determined using a gas chromatograph (GC) (Agilent 7890A, Berkshire, UK) fitted with an electron capture detector with an N_2O detection limit of 0.025 ppmv and a COMBI PAL autosampler (CTC Analytics, Hampshire, UK). GC response was calibrated using certified standard N_2O gas mixtures with N_2O concentrations of 0.35, 1.1, 5.1, and 10.7 ppmv. Subtraction of the mean ambient N_2O concentration from the individual chamber N_2O concentrations after 40 minutes, and assumption of linear accumulation of gas within the chamber allowed the change in concentration for each chamber to be calculated. Along with chamber height, the ideal gas law, air temperature and chamber closure time, this data was used to calculate the individual N_2O flux rate for each chamber. The mean flux from each plot (from the five chambers per plot) was then calculated, and used to derive the mean flux and standard error (SE) for each treatment on every sampling occasion. Plot values were used in all statistical analysis, and annual cumulative fluxes were calculated by interpolating the area under the curve between sampling points. A mean cumulative flux and SE was calculated for each treatment using plot means. The use of a large number of chambers per treatment, combined with the intensive N_2O sampling strategy was designed to take into account the high spatial and temporal variability of N_2O emissions from soils, allowing more reliable estimates of N_2O fluxes from each treatment than has been obtained in similar experiments (e.g. Dobbie and Smith, 2003; Smith et al., 2012).

Ammonia emissions were measured using small-scale wind tunnels and absorption of NH_3 in orthophosphoric acid (Misselbrook et al., 2005b). The wind tunnels were placed at the top of the plots in the direction of the prevailing wind, and positioned to avoid air entering the tunnel from adjacent treated plots. Each wind tunnel consisted of a transparent polycarbonate canopy (2 m x 0.5 m) which was placed over a section of the plot, with air drawn through the canopy at 1 ms^{-1} by a fan in a stainless steel duct. Subsamples of the air from the canopy inlet and outlet were passed through absorption flasks containing 80 ml of 0.02 M orthophosphoric acid. On each sampling occasion the flasks of orthophosphoric acid were changed (after 1, 3 and 6h on the first day and then daily thereafter) and concentrations of NH_3 in inlet and outlet orthophosphoric acid samples were determined (Misselbrook et al., 2005b). One wind tunnel was placed on each manure treatment plot and NH_3 emissions were measured daily for 7 days from CSSB, CSTH and CFYM, and for 14 days from the LM and BL, accounting for expected differences in the timescales of NH_3 emissions from these treatments (Meisinger and Jokela, 2000; Sommer and Hutchings., 2001; Misselbrook et al., 2005a).

2.3. Soil Mineral N

The collection of soil samples coincided with N_2O emission measurements, with samples taken weekly in the month following manure application, and once every four to seven weeks for the remaining period. Measurements were made on one representative bulked sample from each plot, consisting of five random samples from the 0 - 10cm soil layer. The samples were sieved (< 4 mm) and extracted using 2 M KCl and a soil: extractant ratio of 1:2. Plot average soil ammonium (NH_4^+-N) and nitrate (NO_3^--N) contents were determined by colorimetric analysis (Singh et al. 2011), using a Skalar San^{++} continuous flow autoanalyser (Skalar, York, UK).

2.4. Meteorological and additional soil data

A weather station was used to record daily precipitation, and mean and maximum air temperature throughout both experimental periods, with soil temperature (5 cm depth) also measured on each N_2O sampling occasion (RS Components, Northamptonshire, UK). On each N_2O sampling occasion five soil samples (0 - 10 cm depth) were collected from each block and bulked to determine mean block gravimetric moisture content. Metal rings were used to collect and measure soil bulk density before and after ploughing and sowing of the crop in autumn. Soil bulk density values specific to the time of sample collection were then used to convert gravimetric to volumetric moisture contents, and soil water filled pore space (WFPS), assuming a particle density of 2.65 g cm^{-3} (Elliott et al., 1999).

2.5. Crop yield and N uptake

Winter wheat from both experiments was harvested on 5th September 2013 using a small plot harvester, with the yield from a dedicated (untouched) 15 m^2 area recorded for each plot. Additional samples of 100 tillers from each plot were collected by hand to determine the ratio of grain to straw and chaff. The crop yield and the N content and % dry matter (DM) of the grain, straw and chaff was recorded. Grain N content was assumed to be representative of N uptake.

2.6. Emission factor calculations

Annual N_2O EFs were calculated by subtracting the cumulative N_2O emission from the control treatment in each block from the cumulative emission from individual treatments in the same block, as in the IPCC methodology, displayed in Equation 1. A mean EF was then calculated for each treatment.

$$EF = \left(\frac{Cumulative\ N_2O\ flux\ (kg\ N_2O\text{-}N) - cumulative\ N_2O\ flux\ from\ control\ (kg\ N_2O\text{-}N)}{N\ applied\ \ (kg\ N)}\right) \times 100$$

Equation 1.

NH_3 emissions were not measured from the control plots and for the purposes of calculating EFs were assumed to be zero. The calculation of plot mean NH_3 EFs is displayed in Equation 2, with a mean EF then calculated for each treatment.

$$EF = \left(\frac{Cumulative\ NH_3\ flux\ (kg\ NH_3\text{-}N)}{N\ applied\ \ (kg\ N)}\right) \times 100$$

Equation 2.

2.7. Calculation of indirect N_2O emissions

Indirect N_2O emissions from the volatilization of NH_3 and subsequent deposition of NO_3^- or NH_4^+ into terrestrial or aquatic ecosystems were estimated using the assumption that they make up 1 % of the volatilized NH_3-N (IPCC, 2006). Indirect N_2O emissions associated with N leaching losses were also calculated, assuming that 30 % of applied N is lost via leaching, and 0.75 % of the leached N is re-emitted as N_2O (IPCC, 2006).

2.8. Statistical analysis

Statistical analysis was undertaken using GENSTAT (GenStat 16th Edition. Release 16.1., VSN International Ltd., Oxford). The data was analysed to assess the impact of manure type and manure application timing on the following variables: annual N_2O emissions, N_2O EFs, annual NH_3 emissions, NH_3 EFs, total N loss as % N applied, annual direct + indirect N_2O emissions, grain yield, grain N uptake, and yield-scaled emissions. Application of CFYM in only the autumn experiment resulted in an un-balanced experimental design, meaning that two separate data analyses were undertaken: one to assess the impact of manure type, and one to assess the impact of manure application timing. In the first analysis the data was split into autumn and spring experiments (with CFYM included in the autumn analysis), and the effect of manure type was investigated for each season separately using a mixed model and the REML (restricted maximum likelihood) algorithm. The random effect model was block and plot nested within block. The effect of treatment was tested using the Wald statistic. In the second analysis the autumn CFYM data was excluded and the effect of season and any season x treatment interactions were investigated. The effect of season, manure type and their interaction was investigated using a mixed model and the REML algorithm. The random effect model was block nested within season, and plot nested within block nested within season. The effect of season, treatment and their interaction was tested using the Wald statistic. For all analysis the data was transformed if necessary to more closely satisfy the assumption that residuals and random effects are normally distributed. The type of transformation varied depending on which gave the better fit when normality of the residuals was analysed. The data were transformed using Box-Cox transformations (Atkinson, 1985), to determine the most suitable value of lambda to use in the transformation (where a lambda of 1 indicates no transformation, 0 = log transformation and 0.5 = square root transformation). The equations used in the transformations are shown below Tables 2-5 respectively. When data was transformed for statistical analysis both the transformed and back-transformed values are presented in Tables 2-5. The mean and SE for all of the measured variables before data transformation for statistical analysis and removal of outliers are displayed in Supplementary Table 1. Standard error of the difference (SED) values reported in the text are on the transformed scale when data was transformed for analysis. Results were considered statistically significant at $p < 0.05$. If any outliers were identified after the normality of residuals was assessed and these values were considered to be biologically implausible they were removed from the analysis. If biologically plausible and no measurement errors were identified the outliers were retained. The value of -0.90 from control block 1was removed from analysis of spring annual N_2O and direct + indirect N_2O emissions.

3. Results

3.1. Weather, soil moisture and daily N_2O emissions

As the majority of N_2O emissions are thought to occur in the month immediately following application of an N source to soil (Dobbie et al., 1999), rainfall, temperature and soil moisture during this period were assessed, along with conditions throughout the annual experiments. Approximately twice as much rainfall (172 mm) was measured in the first 30 days of the autumn experiment compared to the spring experiment (82.4 mm), with a maximum daily rainfall of 48.6 mm in the first month of the autumn experiment, compared to only 15.6 mm in the spring experiment (Fig.1). In contrast to the month of application, total rainfall over the respective experimental years was greater in the spring (1388 mm) than the autumn experiment (1178 mm), but this was due largely to high and frequent rainfalls in autumn/winter 2013 (Fig.1 b), six months post manure application. Average air temperature in the first 30 days was >1 °C cooler in the autumn experiment (5.6 °C) than the spring (6.8 °C), but on the day of application was higher in autumn (7.7 °C) than spring (1.7 °C) (Fig.1). Average air temperature for the autumn experimental year (7.2 °C) was > 1 °C cooler than the spring experimental year (8.5 °C), due largely to a cold winter in 2012 (Fig.1 a), approximately three months after manure applications. Soil WFPS was closely related to rainfall, with 52 % and 40 % measured on autumn and spring manure application dates, respectively (Fig.1). The large rainfall of 48.6 mm after autumn application, and other further large rainfall events were reflected in an increase in soil WFPS to 59 % on 17th October 2012. Low rainfall in the weeks following spring applications meant that soil WFPS reached a maximum of only 52.1 % on 18th April, falling to very low levels in the summer. This variation in weather and soil conditions between experiments is reflected in the respective experimental N_2O temporal trends and peak emissions. There was a large peak in N_2O from all autumn applications nine days after manure application (Fig.1a), with the greatest emission of 116 g N_2O-N ha^{-1} d^{-1} from CSSB on the day when 48.6 mm of rainfall was recorded. Nitrous oxide emissions were still high (36 g N_2O-N ha^{-1} d^{-1} from CSSB) on 17th October when soil WFPS had reached a maximum. Following spring application N_2O emissions did not demonstrate a single large peak (Fig.1b), with a maximum daily emission of 19.5 g N_2O-N ha^{-1} d^{-1} observed from LM on 19th August 2013, after which all N_2O emissions remained below 5 g N_2O-N ha^{-1} d^{-1} (Fig. 1b).

3.2. Soil mineral N and N_2O emissions

In the autumn experiment an increase in soil NH_4^+-N was observed for all manures on the day of application, peaking on 10th October 2012 under LM and BL, whilst decreasing under other treatments. The highest peak of 24 kg NH_4^+-N ha^{-1} was measured from BL, and the lowest from CFYM (Fig.2a), reflecting its low readily available N content and lack of soil incorporation (Table 1). Background levels were reached on 26th October 2012. Soil NO_3^--N contents also increased after autumn applications, reached a peak between 3rd and 10th October, dropped to lower levels by 16th October, and reached background levels by 3rd December 2012 (Fig.2b). The largest peak of 107 kg NO_3^--N ha^{-1} was measured from the manure with the highest NH_4^+-N content available for nitrification, LM (Table 1) on 10th October 2012. The decrease in soil NO_3^--N between 10th and 16th October corresponded to the N_2O emission peak on 12th October (Fig.2c), reflecting a process of denitrification, at a time of high rainfall and increasing WFPS (Fig.1a). A decrease in soil NO_3^--N from all treatments between 8th November 2012 and 3rd December 2012 corresponded with a small N_2O emission peak on 19th November (Fig.2 b,c), indicating further denitrification.

Although there was a small peak following spring manure applications, soil NH_4^+-N was lower than in the autumn experiment, and the greatest peak of 19 kg NH_4^+-N ha^{-1} was measured from LM 33 days after manure application (Fig.2d). Soil NO_3^--N peaked between 12th April 2013 and 13th May 2013, but was also much lower than in the autumn experiment, with a peak of

57 kg N ha^{-1} from LM 33 days after application (Fig.2e). Further small peaks in NH_4^+-N and NO_3^--N were measured between 29th July 2013 and 19th August 2013, before decreasing to <5 kg N ha^{-1} for the remainder of the experiment. Small peaks in soil mineral N relative to the autumn experiment correspond with much smaller peaks in N_2O (Fig.2f), and also to greater losses of NH_3 in the spring experiment (Fig.3). Small peaks in N_2O immediately after manure application and on 19th August correspond to increases in soil NO_3^--N; however N_2O peaks on 26th June and 29th July correspond with decreasing levels of soil NO_3^--N, indicative of both nitrification and denitrification.

3.3. Ammonia emissions

Emissions of NH_3 following autumn manure applications were greatest in the first hour for all manures apart from BL, which had slightly higher emissions three hours after application. The greatest emission rate of 2.8 kg NH_3-N ha^{-1} hr^{-1} was measured from LM when emissions from CSSB were also high (1.1 kg NH_3-N ha^{-1} hr^{-1}). Emissions from all other manures were < 0.4 kg NH_3-N ha^{-1} hr^{-1} in the first hour after application, and other than the small increase to 0.5 kg NH_3-N ha^{-1} hr^{-1} from BL three hours after application, remained low throughout the measurement period. Emissions from LM remained > 1 kg NH_3-N ha^{-1} hr^{-1} until six hours after application, fell to < 0.2 kg NH_3-N ha^{-1} hr^{-1} 48 hours after application, but remained higher than all other manures for the whole experiment (Fig. 3a). Emissions in the first hour after spring applications were also highest from LM (1.6 kg NH_3-N ha^{-1} hr^{-1}), but were lower than in the autumn experiment. In contrast to the autumn experiment, emission rates from LM, BL and CSSB increased in the first few hours after application, with greatest emissions of 2.7 kg NH_3-N

ha^{-1} hr^{-1} six hours after application from LM. Emissions from all manures declined to < 0.4 kg NH_3-N ha^{-1} hr^{-1} 24 hours after application, with a small increase from LM 72 hours after application (Fig.3b). Although rainfall was much greater over the 14 day measurement period in autumn (83.8 mm) than spring (42.4 mm), the two measurement periods experienced very similar mean air temperatures of 6.2 °C and 6.5 °C, respectively.

3.4 Annual N_2O fluxes and EFs

3.4.1. Manure type

Annual N_2O emissions from the autumn experiment ranged from 0.63 kg N_2O-N ha^{-1} from the control to 2.48 kg N_2O-N ha^{-1} from LM (Table 2), but there were no significant differences between any treatments ($p = 0.083$; standard error of the difference (SED) = 0.56). A significant difference between treatments was however observed in the spring experiment ($p = <0.001$; SED = 0.11), with significantly lower emissions from CSSB and CSTH than all other treatments (Table 2). Annual N_2O EFs for autumn manure applications ranged from 0.27 % for CFYM to 2.17 % for CSSB, with significant differences between treatments ($p = 0.007$; SED = 0.43) (Table 2). The EFs displayed large variation around the IPCC default value of 1 %. In the spring experiment EFs ranged from -1.07 % for CSTH to 0.34 % for BL, but high variability within treatments meant there were no significant differences ($p = 0.408$; SED = 0.83). All of the EFs for spring manure applications were well below the IPCC default of 1 %. The negative EFs measured from CSTH and CSSB in the spring experiment were a consequence of emissions from manure applications often being as small as, or smaller than, emissions from the control. In the spring experiment large variation within EFs was observed when high/low emissions from control plots occurred in the same block as low/high emissions from slurry treatments.

3.4.2. Timing of application

The mean annual N_2O emission from all autumn treatments (2 kg N_2O-N ha^{-1}) was significantly different to that from spring treatments (0.35 kg N_2O-N ha^{-1}) ($p = 0.004$: SED = 0.27). There was no significant season x treatment interaction, indicating that emissions from all manures were significantly greater when applied in autumn than spring (Table 3). There was no significant difference between the mean EFs for autumn and spring applications ($p = 0.145$; SED = 0.99) (Table 3).

3.5. Annual NH_3 fluxes and EFs

3.5.1. Manure type

Cumulative NH_3 emissions in the autumn experiment ranged from 0.7 kg NH_3-N ha^{-1} for CFYM to 39.2 kg NH_3-N ha^{-1} for LM, with a significant difference between treatments (p = <0.001; SED = 1.73) (Table 2). In the spring experiment, cumulative NH_3 emissions ranged from 5.19 kg NH_3-N ha^{-1} from CSTH to 36.4 kg NH_3-N ha^{-1} from LM, and again there was a significant difference between treatments ($p=0.04$; SED=0.53) (Table 2). Annual NH_3 EFs for manures applied in autumn were significantly different between treatments (p = < 0.001; SED = 0.67) (Table 2), and ranged from 0.3 % for CFYM to 16.0 % for LM. Autumn EFs were all much lower than the IPCC default of 20 %. In the spring experiment there were no significant differences in NH_3 EFs between manures ($p = 0.570$; SED = 1.73) (Table 2), and all of the EFs were below the IPCC default value of 20 %.

3.5.2. Timing of application

The only manure with significantly different NH_3 emissions between seasonal experiments was BL, with 17.9 kg NH_3-N ha^{-1} emitted following spring applications, and 3.6 kg NH_3-N ha^{-1} following autumn applications (Table 3). Although the NH_3 EFs were generally greater from spring than from autumn applications, there were no statistically significant differences between seasons ($p = 0.06$; SED = 0.98) (Table 3).

3.6. Total N (NH_3-N + N_2O-N) loss as % N applied

3.6.1. Manure type

In the autumn experiment there was a significant difference in total N loss as a % of N applied between treatments ($p = <0.001$; SED = 0.272), with the greatest emission of 17.1 % N applied from LM, and the lowest of 1.1 % of N applied from CFYM. Total N loss as % N applied was significantly greater from BL than CFYM, but significantly less than from CSSB and CSTH (Table 2). There was no difference between the two slurry treatments (i.e. no effect of application method). Manure type had no significant impact on total N loss as a % of N applied in the spring experiment ($p = 0.56$, SED = 2.24).

3.6.2. Timing of application

There were no statistically significant differences between seasons of manure application ($p = 0.15$; SED = 2.37), and no significant season x treatment interaction ($p = 0.16$; SED = 4.10) (Table 3).

3.7. Direct + Indirect N_2O emissions

3.7.1. Manure type

There was a significant difference between treatments following autumn ($p = 0.02$; SED = 0.527) and spring ($p = <0.001$; SED = 0.09) applications. In the autumn experiment greatest emissions were measured from LM (3.45 kg N_2O-N ha^{-1}) and lowest from the control (Table 2). Following spring applications emissions from LM (1.68 kg N_2O-N ha^{-1}) were significantly greater than all treatments apart from BL (Table 2). Lowest emissions were measured from CSTH (0.03 kg N_2O-N ha^{-1}) but these were not significantly different to those from CSSB.

3.7.2. Timing of application

Mean emissions from all manure treatments were significantly greater in the autumn experiment (2.34 kg N_2O-N ha^{-1}) than the spring experiment (0.69 kg N_2O-N ha^{-1}) ($p = 0.004$; SED = 0.27). This difference between seasons was evident for all types of manure (Table 3).

3.8. Wheat grain yield, yield-scaled emissions and N uptake

3.8.1. Manure type

Grain yields were lower than would usually be expected due to delayed crop sowing caused by unsuitable weather conditions and crop damage from birds. There was a significant difference in grain yields produced from different manures in the autumn ($p = 0.02$; SED = 0.31) and spring ($p = 0.01$; SED = 0.32) experiments (Table 4). In the autumn experiment maximum grain yield (3.48 t ha^{-1}) was produced from BL, and the lowest yield from the control. In the spring experiment maximum yield was produced from LM (5.05 t ha^{-1}) and minimum yield from the control. Yield-scaled emissions from manures applied in autumn ranged from 0.29 kg N_2O-N + NH_3-N t^{-1} grain for the control to 14.45 kg N_2O-N + NH_3-N t^{-1} grain from LM. In the spring experiment these ranged from 0.33 kg N_2O-N + NH_3-N t^{-1} grain from the control to 7.42 kg N_2O-N + NH_3-N t^{-1} grain from LM. A significant difference between treatments was observed in both the autumn ($p = <0.001$; SED = 0.49) and spring ($p = <0.001$; SED = 0.45) experiments (Table 4). There was a significant difference in grain N uptake between manures when applied in autumn ($p = 0.014$; SED = 4.70) and spring ($p = 0.013$; SED = 9.67). In the autumn experiment, this ranged from 31.9 kg N ha^{-1} for the control to 49.7 kg N ha^{-1} for CFYM (Table 4). In the spring experiment grain N uptake from LM (70.6 kg N ha^{-1}) was significantly greater than from all other treatments. Grain N uptake from LM and CSSB was significantly greater than from the control (22.7 kg N ha^{-1}) (Table 4).

3.8.2. Timing of application

For the grain yields, there was a significant season x treatment interaction ($p = 0.01$; SED = 0.23) (Table 5), with only LM producing a significantly higher yield following spring (5.04 t ha^{-1}) compared to autumn (2.91 t ha^{-1}) application. In terms of the yield-scaled emissions, there was also a significant interaction between season and treatment ($p = <0.001$; SED = 0.84), being significantly greater in the autumn experiment than the spring experiment for LM, but significantly lower in the autumn experiment than the spring experiment for BL (Table 5). There was also a significant season x treatment interaction for grain N uptake ($p = 0.015$; SED = 0.42) (Table 5), with only LM producing significantly greater grain N uptake from spring than autumn applications.

4. Discussion

4.1. Timing of application

Wetter conditions observed in the month of autumn applications compared to spring applications in this study reflects 30 year long-term average seasonal differences (78.3 mm: October; 42.5 mm: April), and suggests that livestock manure should be applied in spring if production of N_2O is to be minimised. The observed relationship between N_2O emissions, large rainfall events and increasing soil WFPS does though emphasise that it is the short-term weather after application that is the strongest driver in generating these emissions, and therefore any deviation from seasonal trends may mean that recommendations should be based on weather conditions rather than time of year. As greatest N_2O emissions are expected between a WFPS of 50-70% when denitrification is the dominant N_2O producing process (Davidson, 1991; Dobbie et al., 1999), the higher soil WFPS measured after autumn applications in this study is likely to have promoted greater N_2O emissions when large amounts of NH_4^+ and C were available (Clemens and Huschka, 2001). Although the rainfall in these experiments reflects the long-term seasonal trend of greater precipitation in October than April, the magnitude of rainfall that fell in both months was greater than the long-term average, making it is possible that the N_2O emissions measured here will be larger than those generated in more representative years, a limitation of this one year study. The suggestion to apply manures in drier conditions based on the evidence presented in this study is supported by the reduction in NO_3^- leaching that would also result, with autumn application to agricultural land already restricted in many areas of the UK by NVZ requirements (Defra, 2013; The Scottish Government, 2014). It could be argued that regulations should be more widespread to limit large N_2O emissions outside the NVZ; however enforcement may be controversial due to a lack of required overwinter manure and slurry storage areas (FAS, 2013).

In contrast to N_2O, where soil and weather conditions in the weeks preceding and following manure application may influence emissions, NH_3 emissions are much more influenced by soil and weather conditions on the day of application. Wind speed and DM content have been identified as important influencing factors in generating NH_3 emissions from slurry (Sommer et al., 2003; Misselbrook et al., 2005a), as well as the soil surface conditions which influence the rate of infiltration (Sommer et al., 2003; Misselbrook et al., 2005c). For solid manures, rainfall after application is the most important factor, although the effect can vary depending on timing, duration and intensity (Misselbrook et al., 2005a). Rainfall during the first 48 hours after application in the present study was very low for both experiments (4.2 mm in autumn and 0.8 mm in spring). Air temperature has often demonstrated a strong influence on emissions (Sommer and Olesen, 1991; Meisinger and Jokela, 2000), and although the two experiments had similar mean air temperatures over the 14 days of measurement, the temperature in the 48 hours after applications was much lower in spring (2.1°C) than autumn (7.6 °C) (Fig.1). The fact that air temperature did not exceed 8 °C at the time of application in either experiment could help explain the lack of significant differences between experiments. Wind speed and humidity were not measured in these experiments, but are variables that could also play an important role (Brunke et al., 1988). This study has shown that it is very short-term weather conditions that have the biggest control on NH_3 emissions, suggesting that decisions regarding the timing of application should perhaps be dictated by short-term weather rather than calendar season. These results also demonstrate the requirement to consider both forms of gaseous N loss in decisions regarding when to apply livestock manures, and the importance of including NH_3 measurements in addition to N_2O. When emissions from both experiments are compared as a % of the N applied (Table 3), the significantly greater direct and indirect N_2O emissions from autumn applications are counteracted by greater NH_3 emissions in spring.

Incorporation of the manures into the soil in the autumn experiment, compared to top-dressing in the spring could also help to explain higher annual N_2O emissions from autumn applications. This will have provided soil microorganisms rapid access to manure N and increased soil moisture, both of which promote N_2O production. Manures applied in spring remained on the soil surface for longer, and would be less accessible to soil microorganisms (Wulf et al., 2001; Velthof et al., 2003; Perala et al., 2006; Rodhe et al., 2006) and more prone to NH_3 volatilisation, supported by the lower soil NH_4^+-N levels measured in spring. Although NH_3 emissions were generally higher from manures applied in spring, BL was the only treatment to show a significant difference. This could be explained by the higher readily available N content (Table 1) of the BL applied in spring (Defra, 2010); however this would also have been expected to increase N_2O emissions. The significantly greater NH_3 emissions in the spring are unlikely to be the result of top-dressing the spring applications, as the manures were not incorporated into the soil in the autumn experiment until 24 hours after application, by which time NH_3 emissions had already declined to very low levels (Fig.3). To be an effective mitigation method soil incorporation should therefore be undertaken very soon after application.

Although the application of manures to bare soil in the autumn experiment generated greater losses of N_2O than when manures were applied to a growing crop in the spring experiment, higher grain N uptake in the spring experiment compared to the autumn experiment was only measured for LM. Higher N uptake, as demonstrated by Limaux et al. (1999), did not occur under the other manures and it is unlikely therefore, that crop N uptake influenced N_2O or NH_3 emissions. The general lack of difference in crop yield between autumn and spring experiments, combined with generally greater N_2O emissions after autumn application and greater NH_3 emissions after spring application produced similar yield-scaled emissions for most autumn and spring applications. Season of manure application thus had no effect on the amount of emissions per unit of yield obtained.

4.2. Manure type:

Although annual N_2O emissions did not differ significantly between any of the manures applied in the autumn experiment, it must be realised that the total N applied varied between manures (Table 1). It is possible that high N_2O emissions from cattle slurry with a low N application rate could be the result of its low DM content (Table 1), which may have increased soil moisture and N_2O production by denitrification (Davidson, 1992). Although soil WFPS remained below the denitrification “threshold” of 60%, localised hotspots (WFPS >60%) are likely to have occurred within the soil volume. Significantly lower emissions from CSSB and CSTH than from the other manures in the spring experiment does though suggest that applying manures with a lower N content can reduce N_2O emissions. Comparison of N_2O EFs takes N application rate into account, and the lack of a significant difference between spring EFs, and a significant difference between autumn EFs reflects the annual N_2O emission results.

In relation to $NH_{3,}$ the significantly greater cumulative emissions measured from LM than all other manures in both experiments can be explained not only by higher peak emissions, but also by the longer timescale over which emissions occurred (Fig.3). This is thought to result from the high N application rate and NH_4^+-N content of LM promoting NH_3 production, along with the slow breakdown of uric acid and conversion to urea, followed by urea hydrolysis to ammonium (Misselbrook et al., 2000; Sommer and Hutchings, 2001). Manures with a low DM content also infiltrate faster into the soil (Menzi et al., 1997; Chambers et al., 1999) which could explain the smaller losses of NH_3 from the high moisture content slurries compared to the solid manures. The lack of any significant differences in N_2O and NH_3 emissions between CSSB and CSTH demonstrates that method of slurry application had no effect on either flux, in contrast to research where 30-70% lower NH_3 emissions were measured from CSTH than CSSB (Pain and Misselbrook, 1997; Webb et al., 2010). The low DM content of the cattle slurry used in this experiment may have reduced the effectiveness of the CSTH treatment in lowering NH_3 emissions, as slurry DM content can influence the degree to which it remains in bands after trailing hose application, and therefore the extent to which the emitting surface area is minimised. Additionally, trailing hose application is more effective in reducing NH_3 emissions when a crop canopy is present (Thorman et al., 2008), which was not the case for the autumn application. Similarly, although the crop was established at the time of spring application, there had been very little canopy development.

The impact of manure type on grain yield and N uptake was evident in the spring experiment, where the highest grain yield and N uptake were measured in winter wheat treated with LM. This manure had the highest NH_4^+-N content and N application rate in both experiments; however the higher yield and N uptake were not observed following autumn applications. This was most likely due to the much greater loss of NH_3 from LM applications relative to other fertilisers in autumn, leading to less N being available for crop uptake. The lowest yield-scaled emissions in the autumn experiment measured from CFYM and BL indicate that these manures generate the lowest N_2O and NH_3 emissions whilst maximising grain yield, but the lowest yield-scaled emissions measured in the spring experiment from CSSB and CSTH emphasise the variation caused by time of manure application. Layer manure did however produce the highest yield-scaled emissions at both times of application.

4.3. Comparison to previously reported EFs and the IPCC default EFs

The large variation in EFs reported in this study from different types of livestock manure, and from the same type of manure applied at different times (Table 3), supports the findings of previous research. Nitrous oxide EFs for CSSB of 2.57% when applied in autumn, and - 0.90% when applied in spring, demonstrate considerable variation in EFs for the same manure depending on the timing of application. This adds support to the large variation in EFs reported for dairy cow slurry in Chadwick et al. (2000) and Velthof and Mosquera (2011), ranging from 0.12% to 0.97%. The high variability in N_2O EFs measured in this study means they are neither consistently higher nor lower than those reported elsewhere. Autumn and spring LM EFs of 0.77 % and 0.20 %, respectively, are much smaller than the 2.40 % reported in Webb et al. (2014), compared to autumn and spring BL EFs of 1.08 % and 0.36 % respectively, which are much greater than the 0.05 % reported in Chadwick et al. (2000). The EF of 0.27% measured in this study for CFYM is in the range (0.09% - 0.55%) reported from two English sites in Webb et al. (2014). The identification of large variation in EFs, both within this study and within the literature, suggests that environmental variables, soil type, soil conditions and manure properties can have a large impact on emissions. There is a clear requirement for EFs to account for these environmental and soil variables, and to account for the type of manure applied. The mean EF of 1.72 % for autumn manure applications is larger than the IPCC default of 1 %, suggesting that the recently adjusted value of 1.25 % (IPCC, 2006) was perhaps more appropriate, however the mean EF of - 0.33 % from spring applications is much lower than the 1 % default. This research demonstrates that weather conditions following autumn and spring applications could be markedly different, making it inappropriate to use a single EF value for all types of manure and periods of application.

NH_3 EFs measured in this study were also highly variable and often higher than those reported in the literature, but lower than the IPCC default value of 20 %. Surface spreading of cattle slurry produced EFs ranging from 8.2 % - 18.6 %, greater than the 6 - 12 % reported in Van der Hoek (1998), and LM EFs of 16 % reported here are much larger than the 0.15 % and 7 % reported in Van der Hoek (1998) and Sommer and Hutchings (2001) respectively. All of the NH_3 EFs measured in this study from both seasons of application were lower than the IPCC default value of 20 %, despite the different weather conditions. This suggests that use of the default IPCC EF could overestimate NH_3 emissions from manures applied under these environmental conditions, and that using country-specific EFs for manure applications in the UK NH_3 emission inventory may be more appropriate.

5. Conclusion

The results of this research demonstrate how manure type and the time of its application can influence N_2O and NH_3 emissions, and that the trade-off between N_2O and NH_3 emissions could be crucial in deciding on timing and method of application for different manure types. The variation in the extent of emissions from different types of manure demonstrates the effects of manure properties such as moisture content, total N and available N content on emission generation. Emissions of N_2O were strongly affected by the timing of manure application, reflecting the effects of weather conditions, manure incorporation and crop growth on production of N_2O, with greatest N_2O emissions measured from manures applied and incorporated into bare soil in warmer and wetter autumn conditions. Although not significantly different between seasons, emissions of NH_3 were conversely greater from manures applied in spring. Crop yield was generally unaffected by manure application timing or manure type, but yield scaled emissions were significantly greater from LM than all other manure types. There was high variability in N_2O and NH_3 EFs, dependent on manure type and application timing, and large deviation from the IPCC default EF values for N_2O and NH_3 emissions. This highlights the requirement for N_2O and NH_3 EFs to take into account the effect of manure type and timing of application in order to improve the accuracy of national inventories of N_2O and NH_3 emission. Future research is needed to determine whether the results obtained from this work are applicable to different geographical areas, and to take into account the loss of N via leaching.

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Table 1. Manure properties and application rates for autumn and spring experiments. ND = not detectable; NM = not measured. The same cattle slurry was used in the ‘cattle slurry trailing hose’ and ‘cattle slurry surface broadcast’ treatments

Treatment	Time of application	Incorporated/ top-dressed	Fertiliser application rate (t ha^{-1})	Total N application rate (kg N ha^{-1})	Readily available N (kg N ha^{-1})			Total C application rate (kg C ha^{-1})	C:N ratio	Dry Matter (%)	pH
					NH_4^+-N	NO_3^--N	Uric acid-N				
Broiler litter	Autumn	Incorporated	5.69	141	12.1	ND	NM	862	6.1	41.6	8.3
	Spring	Top-dressed	8.06	121	22.6	ND	1.9	729	6.0	26.6	8.9
Layer manure	Autumn	Incorporated	14.6	244	120.3	ND	NM	1001	4.1	21.8	8.0
	Spring	Top-dressed	16.4	228	91.3	ND	6.1	1111	4.9	21.8	8.6
Cattle slurry	Autumn	Incorporated	41.7	62.5	30.4	ND	NM	334	5.4	2.30	6.8
	Spring	Top-dressed	41.7	50	22.1	ND	NM	289	5.8	2.23	6.9
Cattle FYM	Autumn	Top-dressed	29.7	175	5.3	3.3	NM	2007	11.5	18.4	8.4

Table 2. The impact of manure type on annual cumulative N_2O emissions, N_2O EFs, cumulative NH_3 emissions, NH_3 EFs, total N loss as % N applied, and annual direct + indirect N_2O emissions when applied in autumn and spring respectively: Transformed (Tr) and back transformed (Back Tr) values. When a significant effect between fertilisers is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Season-Treatment	Cumulative N_2O emissions (kg N_2O-N ha^{-1})		N_2O EF (%)		Cumulative NH_3 emissions (kg NH_3-N ha^{-1})#		NH3 EF (%)		Total N loss as % N applied		Annual direct + indirect N_2O (kg N_2O-N ha^{-1})	
	Tr^{1}	Back Tr	Tr^{2}	Back Tr			Tr^{3}	Back Tr	Tr^{4}	Back Tr	Tr^{5}	Back Tr
A-Con	-0.40	0.63	-	-	-		-	-	-	-	-0.40^{a}	0.63
A-BL	1.05	2.20	0.06^{bc}	1.07	3.60^{ab}		1.13^{b}	2.54	2.05^{b}	4.10	1.32^{bc}	2.55
A-LM	1.27	2.48	-0.56^{ab}	0.56	39.23^{c}		5.08^{d}	16.02	6.28^{d}	17.14	1.97^{c}	3.45
A-CSSB	1.10	2.26	0.80^{c}	2.17	5.54^{b}		3.25^{c}	8.14	4.96^{c}	12.11	1.26^{bc}	2.47
A-CSTH	1.09	2.25	0.70^{c}	1.96	5.33^{b}		3.28^{c}	8.02	4.91^{c}	11.94	1.24^{bc}	2.44
A-CFYM	0.27	1.28	-1.22^{a}	0.27	0.69^{a}		-0.97^{a}	0.29	0.09^{a}	1.09	0.62^{ab}	1.67
LSD	NS		1.00		4.00		1.55		1.27		1.18	
	Tr^{6}	Back Tr	Tr^{7}	Back Tr	Tr^{8}	Back Tr	Tr^{9}	Back Tr	Tr^{10}	Back Tr	Tr^{11}	Back Tr
S-Con	0.66^{b}	0.95	-	-	-	-	-	-	-	-	0.58^{b}	0.90
S-BL	0.54^{b}	0.74	2.19	0.34	3.88^{b}	17.67	6.69	14.69	8.23	15.34	0.71^{bc}	1.20
S-LM	0.57^{b}	0.79	2.08	0.20	5.26^{c}	36.38	7.15	16.06	8.71	16.44	0.88^{c}	1.68
S-CSSB	-0.14^{a}	-0.08	1.08	-1.02	2.76^{ab}	9.00	7.95	18.56	9.64	18.63	0.08^{a}	0.13
S-CSTH	-0.15^{a}	-0.09	1.04	-1.07	1.95^{a}	5.19	5.45	11.24	6.36	11.28	0.03^{a}	0.08
LSD	0.26		NS		1.30		NS		NS		0.21	

Transformations of non-normal data for statistical analysis: [1]((kgN_2O**0.7)-1)/0.7 [2]((N_2O EF**0.1)-1)/0.1 [3]((NH_3 EF**0.4)-1)/0.4 [4]((Total N loss as %N applied**0.5)-1)/0.5 [5]((Direct + indirect N_2O**0.7)-1)/0.7 [6]((kgN_2O + 0.95)**0.1)-1)/0.1 [7]((N_2O EF + 3.2)**0.8)-1)/0.8 [8]((kgNH_3**0.2)-1)/0.2 [9]((NH_3 EF**0.6)-1)/0.6 [10]((Total N loss as %N applied**0.7)-1)/0.7 [11]((Direct + indirect N_2O + 0.95**-0.2)-1)/-0.2

no transformation required

Table 3. The impact of season of application, manure type and their interactions on annual cumulative N_2O emissions, N_2O EFs, cumulative NH_3 emissions, NH_3 EFs, total N loss as % N applied, and annual direct + indirect N_2O emissions. Transformed (Tr) and back transformed (Back Tr) values. When a significant effect is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

	Cumulative N_2O emissions (kg N_2O-N ha^{-1}) #	N_2O EF (%)		Cumulative NH_3 emissions (kg NH_3-N ha^{-1}) #	NH_3 EF (%)		Total N loss as % N applied#	Annual direct + indirect N_2O (kg N_2O-N ha^{-1}) #
		Tr^1	Back Tr		Tr^2	Back Tr		
Autumn	2.00^a	3.55	1.72	13.42	4.23	8.21	11.44	2.34^a
Spring	0.35^b	1.76	-0.33	17.58	6.81	15.04	15.71	0.69^b
Con	0.51	-	-	-	-	-	-	0.51^a
BL	1.48	2.68	0.71	10.73^a	3.97^a	7.62	9.75	1.89^{bc}
LM	1.68	2.48	0.48	38.05^b	7.15^b	16.06	16.82	2.59^c
CSSB	1.12	2.76	0.80	7.56^a	$6.12a^b$	13.06	15.75	1.33^{ab}
CSTH	1.10	2.71	0.74	5.67^a	4.83^a	9.65	11.97	1.28^{ab}
A-Con	0.68	-	-	-	-	-	-	0.68
S-Con	0.33	-	-	-	-	-	-	0.33
A-BL	2.20	3.00	1.08	3.60^a	1.25	2.54	4.11	2.55
S-BL	0.77	2.37	0.36	17.85^b	6.69	14.69	15.39	1.22
A-LM	2.55	2.73	0.77	39.23^c	7.14	16.03	17.12	3.50
S-LM	0.80	2.23	0.20	36.86^c	7.15	16.06	16.52	1.68
A-CSSB	2.31	4.27	2.57	5.54^a	4.30	8.38	12.46	2.51
S-CSSB	-0.06	1.24	-0.90	9.59^a	7.95	18.56	19.05	0.15
A-CSTH	2.27	4.22	2.51	5.33^a	4.22	8.19	12.07	2.47
S-CSTH	-0.08	1.20	-0.94	6.01^a	5.45	11.24	11.87	0.09
Season LSD	0.75	NS		NS	NS		NS	0.75
Treatment LSD	NS	NS		5.17	2.18		NS	0.93
Season*treatment LSD	NS	NS		7.46	NS		NS	NS

Transformations of non-normal data for statistical analysis ^{1}(((kg N_2O+0.95)**0.6)-1)/0.6 ^{2}((NH_3 EF**0.6)-1)/0.6 # no transformation required

Table 4. The impact of manure type on grain yield, N_2O and NH_3 yield intensity, and grain N uptake when applied in autumn and spring, respectively: Transformed (Tr) and back transformed (Back Tr) values. When a significant effect between fertilisers is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Season-Treatment	Grain yield @ 85% DM ($t\ ha^{-1}$)#		$N_2O + NH_3$ yield intensity (kg N_2O-N and NH_3-N t^{-1} grain DM)#	Grain N uptake (kg N ha^{-1})#
A-Con	2.38^{a}		0.29^{a}	31.86^{a}
A-BL	3.48^{c}		1.67^{b}	48.72^{bc}
A-LM	2.90^{abc}		14.45^{e}	38.83^{ab}
A-CSSB	2.45^{a}		3.32^{d}	33.37^{a}
A-CSTH	2.77^{ab}		2.74^{c}	39.31^{abc}
A-CFYM	3.37^{bc}		0.59^{a}	49.70^{c}
LSD	0.69		1.09	10.48
	Tr[1]	Back Tr		
S-Con	0.60^{a}	1.71	0.33^{a}	22.70^{a}
S-BL	1.35^{b}	2.94	6.43^{c}	41.60^{ab}
S-LM	2.28^{c}	5.05	7.42^{c}	70.60^{c}
S-CSSB	1.61^{bc}	3.47	2.83^{b}	48.00^{b}
S-CSTH	1.33^{b}	2.91	2.08^{b}	40.30^{ab}
LSD	0.72		1.04	22.34

Transformations of non-normal data for statistical analysis: [1]((grain yield**0.4)-1)/0.4 # no transformation required

Table 5. The impact of season of application, manure type and their interactions on grain yield, N_2O and NH_3 yield intensity, and grain N uptake: Transformed (Tr) and back transformed (Back Tr) values. When a significant effect is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

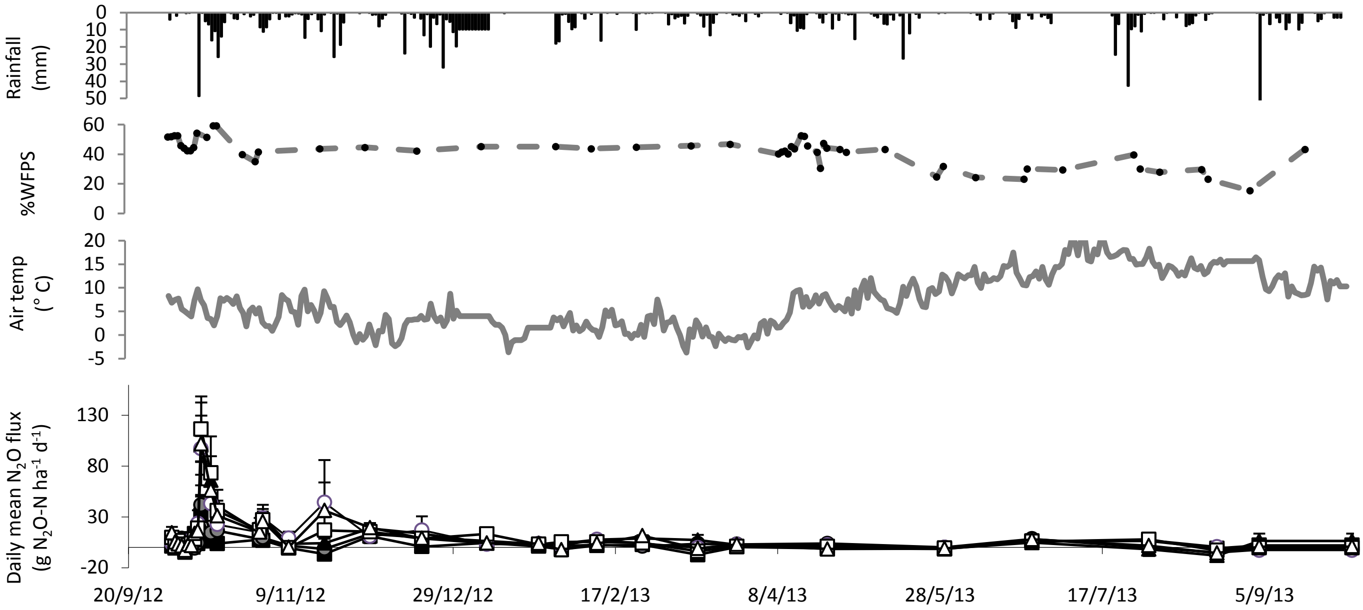
	Grain yield @ 85% DM (t ha^{-1})		N_2O + NH_3 yield intensity (kg N_2O-N and NH_3-N t^{-1} grain DM) #	Grain N uptake (kg N ha^{-1})	
	Tr[1]	Back Tr		Tr[2]	Back Tr
Autumn	1.12	2.75	4.49	5.34	37.82
Spring	1.25	3.05	3.82	5.53	41.35
Con	0.75^{a}	2.01	0.31^{a}	4.62^{a}	26.36
BL	1.31^{bc}	3.20	4.05^{c}	5.70^{bc}	44.88
LM	1.55^{c}	3.86	10.93^{d}	6.04^{c}	52.48
CSSB	1.17^{b}	2.86	3.07^{b}	5.37^{b}	38.37
CSTH	1.15^{b}	2.82	2.41^{b}	5.43^{b}	39.50
A-Con	0.93^{ab}	2.35	0.29^{a}	4.96^{ab}	31.37
S-Con	0.56^{a}	1.70	0.33^{a}	4.28^{a}	22.02
A-BL	1.42^{c}	3.49	1.67^{ab}	5.88^{cd}	48.79
S-BL	1.20^{bc}	2.93	6.43^{c}	5.52^{bc}	41.23
A-LM	1.19^{bc}	2.91	14.45^{d}	5.39^{bc}	38.75
S-LM	1.91^{d}	5.04	7.42^{c}	6.70^{d}	70.16
A-CSSB	0.96^{abc}	2.41	3.32^{b}	5.07^{abc}	33.14
S-CSSB	1.38^{bc}	3.38	2.83^{b}	5.67^{bc}	44.26
A-CSTH	1.12^{bc}	2.75	2.74^{b}	5.39^{bc}	38.75
S-CSTH	1.19^{bc}	2.91	2.08^{ab}	5.46^{bc}	40.07
Season LSD	NS		NS	NS	
Treatment LSD	0.32		0.81	0.57	
Season*treatment LSD	0.49		1.87	0.89	

Transformations of non-normal data for statistical analysis: [1] ((grain yield**0.2)-1)/0.2 [2] ((grain N uptake**0.2)-1)/0.2 # no transformation required

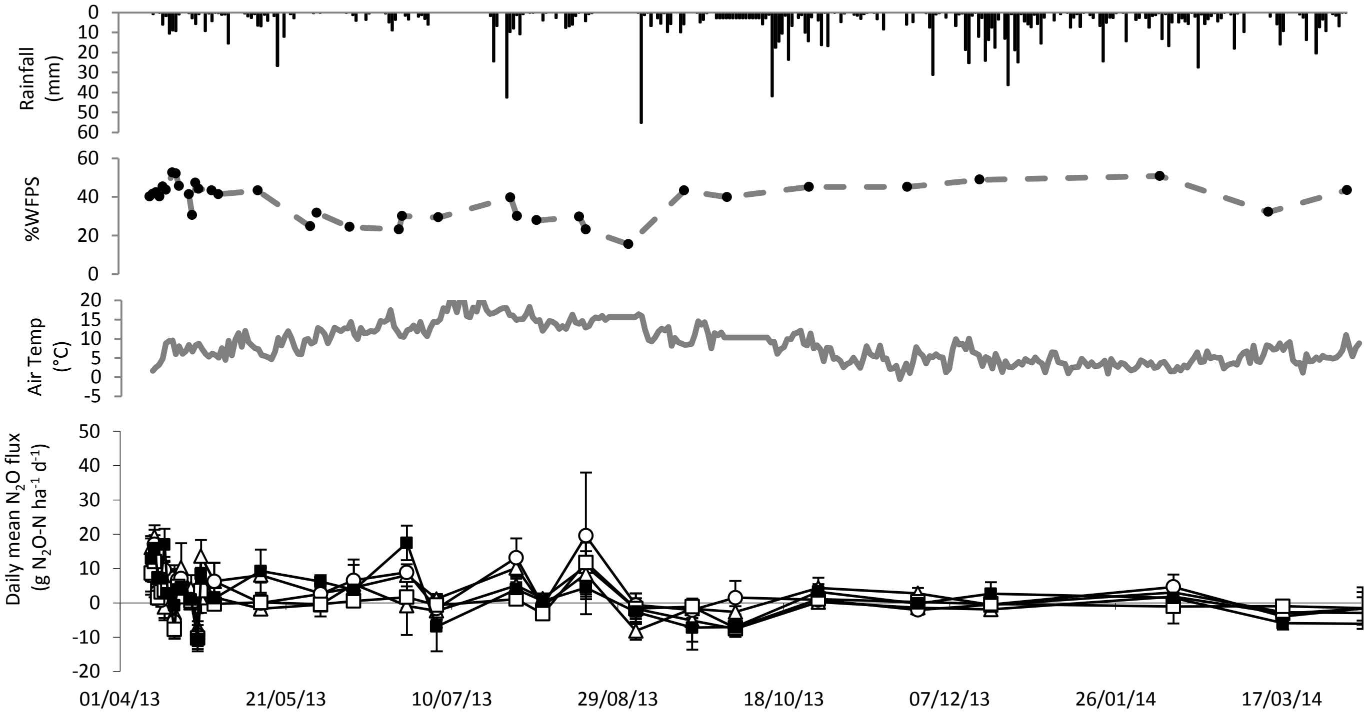
Supplementary Table 1. The mean and standard error (SE) (n = 3) of annual cumulative N_2O emissions, N_2O emission factors (EFs), cumulative NH_3 emissions, NH_3 EFs, total N loss as % N applied, annual direct + indirect N_2O, grain yield, N_2O + NH_3 yield intensity, and grain N uptake before data transformation for statistical analysis. Treatment rates and manure composition data are displayed in Table 1. A = autumn application; S = spring application; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose; CFYM = cattle farmyard manure

		Cumulative N_2O (kg N_2O-N ha^{-1})		N_2O EF (%)		Cumulative NH_3 (kg NH_3-N ha^{-1})		NH_3 EF (%)		Total N loss as % N applied		Annual direct + indirect N_2O (kg N_2O-N ha^{-1})		Grain yield @ 85% DM (t ha^{-1})		N_2O + NH_3 yield intensity (kg N_2O-N and NH_3-N t^{-1} grain DM)		Grain N uptake (kg N ha^{-1})	
		Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
A	Con	0.68	0.29	-	-	-	-	-	-	-	-	0.68	0.29	2.38	0.31	0.29	0.13	31.86	4.56
	BL	2.20	0.12	1.08	0.12	3.60	0.35	2.55	0.24	4.11	0.29	2.55	0.13	3.48	0.05	1.67	0.14	48.72	0.62
	LM	2.55	0.83	0.77	0.46	39.23	1.48	16.03	0.60	17.12	0.41	3.50	0.82	2.90	0.16	14.45	0.50	38.83	2.73
	CSSB	2.31	0.61	2.59	0.96	5.54	2.17	8.86	3.47	12.46	2.93	2.51	0.60	2.45	0.34	3.32	0.77	33.37	3.32
	CSTH	2.27	0.47	2.53	1.15	5.33	1.58	8.53	2.52	12.07	1.78	2.47	0.45	2.77	0.26	2.74	0.29	39.31	5.36
	CFYM	1.28	0.04	0.34	0.16	0.69	0.44	0.39	0.25	1.12	0.27	1.68	0.05	3.37	0.10	0.59	0.16	49.70	3.71
S	Con	0.33	0.70	-	-	-	-	-	-	-	-	0.33	0.70	1.75	0.31	0.33	0.53	22.70	4.10
	BL	0.77	0.21	0.36	0.49	17.85	1.96	14.75	1.62	15.39	1.53	1.22	0.20	2.94	0.23	6.43	0.85	41.61	4.84
	LM	0.80	0.11	0.21	0.30	36.86	4.60	16.17	2.02	16.52	2.06	1.68	0.16	5.06	0.32	7.42	0.66	70.59	6.84
	CSSB	-0.06	0.13	-0.79	1.51	9.59	2.83	19.18	5.66	19.05	5.41	0.15	0.10	3.64	0.99	2.83	0.65	48.00	13.77
	CSTH	-0.08	0.10	-0.83	1.49	6.01	2.37	12.03	4.75	11.87	4.71	0.09	0.10	2.90	0.06	2.08	0.86	40.34	3.13

Figure 1.



a.



b.

—■— Con —●— CFYM —▲— BL —○— LM —□— CSSB —△— CSTH

Figure 2.

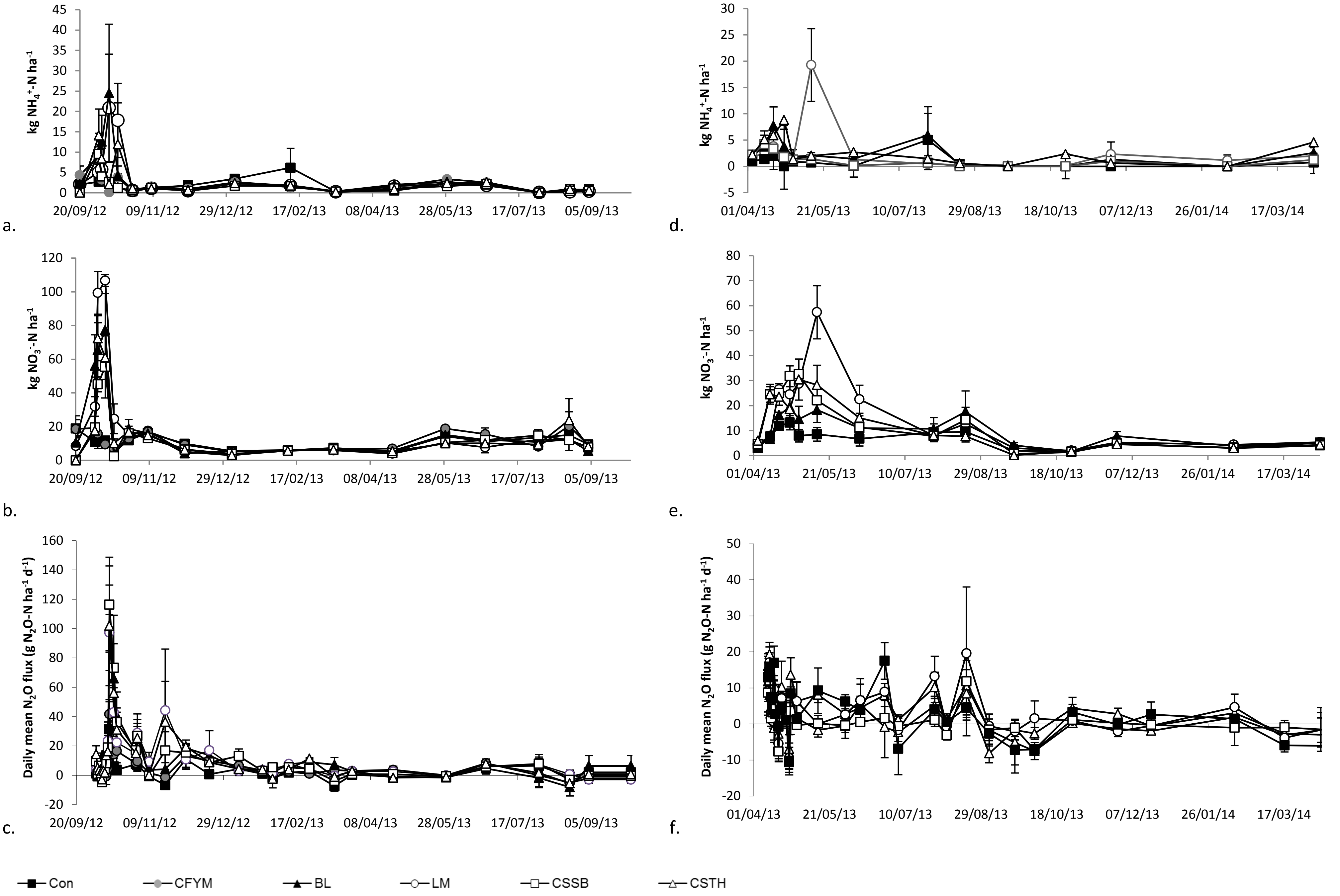

kg NH$_4^+$-N ha^{-1}
45
40
35
30
25
20
15
10
5
0
20/09/12
09/11/12
29/12/12
17/02/13
08/04/13
28/05/13
17/07/13
05/09/13
a.
kg NO$_3^-$-N ha^{-1}
120
100
80
60
40
20
0
20/09/12
09/11/12
29/12/12
17/02/13
08/04/13
28/05/13
17/07/13
05/09/13
b.
Daily mean N$_2$O flux (g N$_2$O-N ha^{-1} d^{-1})
160
140
120
100
80
60
40
20
0
-20
20/09/12
09/11/12
29/12/12
17/02/13
08/04/13
28/05/13
17/07/13
05/09/13
c.
kg NH$_4^+$-N ha^{-1}
30
25
20
15
10
5
0
-5
01/04/13
21/05/13
10/07/13
29/08/13
18/10/13
07/12/13
26/01/14
17/03/14
d.
kg NO$_3^-$-N ha^{-1}
80
70
60
50
40
30
20
10
0
01/04/13
21/05/13
10/07/13
29/08/13
18/10/13
07/12/13
26/01/14
17/03/14
e.
Daily mean N$_2$O flux (g N$_2$O-N ha^{-1} d^{-1})
50
40
30
20
10
0
-10
-20
01/04/13
21/05/13
10/07/13
29/08/13
18/10/13
07/12/13
26/01/14
17/03/14
f.
Con
CFYM
BL
LM
CSSB
CSTH

Figure 3.

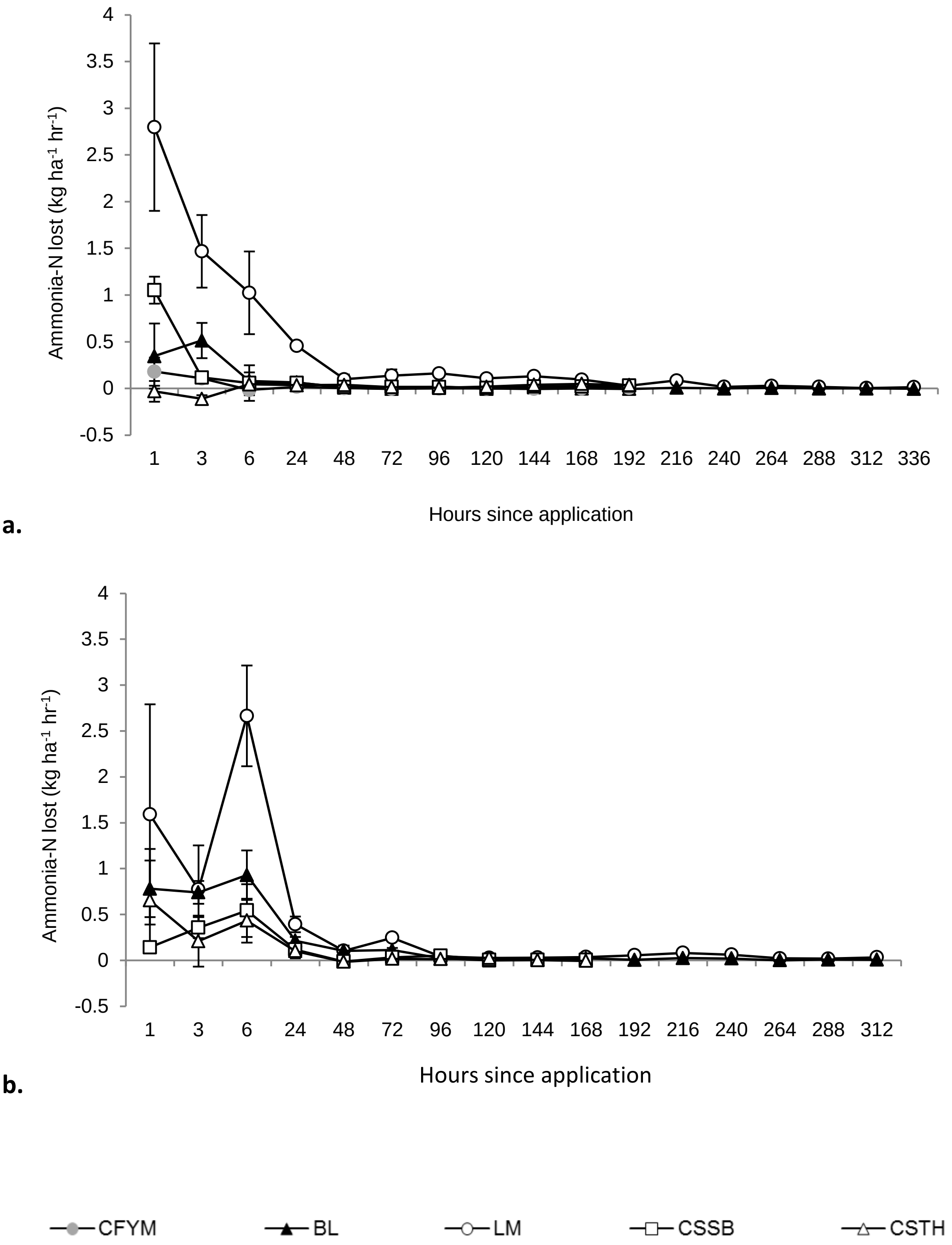

Ammonia-N lost (kg ha^{-1} hr^{-1})
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
1
3
6
24
48
72
96
120
144
168
192
216
240
264
288
312
336
Hours since application
a.
Ammonia-N lost (kg ha^{-1} hr^{-1})
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
1
3
6
24
48
72
96
120
144
168
192
216
240
264
288
312
Hours since application
b.
CFYM
BL
LM
CSSB
CSTH

Figure captions

Fig.1. Variation in daily rainfall, soil water filled pore space (%WFPS) and air temperature throughout the experimental periods, and their relationship with daily N_2O emissions. **a.** autumn experimental year; **b.** spring experimental year. Error bars on the N_2O data indicate the SE of the mean, n = 3. LM = layer manure; CFYM = cattle farmyard manure; CSSB = cattle slurry surface broadcast; Con = control; BL = broiler litter; CSTH = cattle slurry trailing hose

Fig.2.a. Variation in soil NH_4^+-N following manure application in autumn. **b.** Variation in soil NO_3^--N following manure application in autumn **c.** daily N_2O emissions following manure application in autumn. **d.** Variation in soil NH_4^+-N following manure application in spring **e.** Variation in soil NO_3^--N following manure application in spring **f.** daily N_2O emissions following manure application in spring. Error bars indicate the standard error of the mean (n = 3). LM = layer manure; CFYM = cattle farmyard manure; CSSB = cattle slurry surface broadcast; Con = control; BL = broiler litter; CSTH = cattle slurry trailing hose. Note – use of different scales on the Y axis in the autumn (a, b, c) and spring (d, e, f) graphs to provide clarity of soil mineral N and N_2O flux data

Fig.3. The variation in NH_3 emissions following manure applications (LM = layer manure; CFYM = cattle farmyard manure; CSSB = cattle slurry surface broadcast; Con = control; BL = broiler litter; CSTH = cattle slurry trailing hose) to arable land in autumn and spring. **a.** autumn experiment; **b.** spring experiment. Error bars on the NH_3 data indicate the SE of the mean, n = 3.