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# Nitrous oxide emission sources from a mixed livestock farm

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## Abstract

The primary aim of this study was to identify and compare the most significant sources of nitrous oxide ($N_2O$) emissions from soils within a typical mixed livestock farm in Scotland. The farm area can be considered as representative of agricultural soils in this region where outdoor grazing forms an important part of the animal husbandry. A high temporal resolution dynamic chamber method was used to measure $N_2O$ fluxes from the featureless, general areas of the arable and pasture fields (general) and from those areas where large nitrogen additions are highly likely, such as animal feeding areas, manure heaps, animal barns (features). Individual $N_2O$ flux measurements varied by four orders of magnitude, with values ranging from -5.5 to 80,000 µg $N_2O$-N $m^{-2}$ $h^{-1}$. The log-normal distribution of the fluxes required the use of more complex statistics to quantify uncertainty, including a Bayesian approach which provided a robust and transparent method for "upscaling" i.e. translating small-scale observations to larger scales, with appropriate propagation of uncertainty. Mean $N_2O$ fluxes associated with the features were typically one to four orders of magnitude larger than those measured on the general areas of the arable and pasture fields. During warmer months, when widespread grazing takes place across the farm, the smaller $N_2O$ fluxes of the largest area source - the general field (99.7% of total area) - dominated the overall $N_2O$ emissions. The contribution from the features should still be considered important, given that up to 91 % of the fluxes may come from only 0.3 % of the area under certain conditions, especially in the colder winter months when manure heaps and animal barns continue to produce emissions while soils reach temperatures unfavourable for microbial activity (< 5 ℃).

**Keywords:** Farm scale, greenhouse gas, upscaling, nitrogen

## 1. Introduction

Nitrous oxide ($N_2O$) is a powerful greenhouse gas, which also contributes to stratospheric ozone depletion (Intergovernmental Panel on Climate Change, 2014; Ravishankara et al., 2009). Microbially mediated nitrification and denitrification pathways in soils and aquatic environments are the primary sources of $N_2O$ (Butterbach-Bahl et al., 2013; Davidson et al., 2000). The increase in livestock numbers (Thornton, 2010) and large-scale application of nitrogen fertilisers to agricultural soils over the past 100 years have contributed to large increases in concentrations of reactive nitrogen in the environment (Fowler et al., 2013). This has resulted in a significant increase in anthropogenic $N_2O$ emissions at a global scale (Reay et al., 2012).

Quantifying agricultural $N_2O$ emissions at large scales has proven difficult due to the uncertainties involved in measuring $N_2O$ fluxes (Cowan et al., 2015; Giltrap et al., 2014; Mathieu et al., 2006), the multiple environmental factors which influence $N_2O$ production at a microbial level (Butterbach-Bahl et al., 2013; Thomson et al., 2012) and in accounting for the effects of a wide variety of farm management practices which alter the natural nitrogen cycle. The complex heterogeneous nature of agricultural soils presents a challenge when it comes to identifying which microbiological processes (i.e. denitrification, nitrifier denitrification, chemodenitrification, nitrification) are contributing to $N_2O$ emissions. These processes may occur simultaneously within microsites of the same soil (Baggs, 2008), the rates of which may be independently controlled by a multitude of different environmental factors (e.g. temperature, soil moisture content, availability of organic carbon) (Bateman and Baggs, 2005; Davidson, 1992). The availability of mineralised nitrogen (predominantly ammonium $NH_4^+$ and nitrate $NO_3^-$) is known to be a significant driver of $N_2O$ production from agricultural soils, but this relationship is unpredictable and can be influenced significantly by a wide spectrum of spatial and temporal environmental variables (Cowan et al., 2015; Kim et al., 2013; Shcherbak et al., 2014).

Previous experiments have been carried out with the goal of quantifying $N_2O$ emissions from individual farms with some success (Brown et al., 2001; Ellis et al., 2001; Flessa et al., 2002; Velthof and Oenema, 1997). Due to the complexity and magnitude of the task, these studies often focus on a particular aspect of $N_2O$ emissions from agricultural sources such as animal waste management (Chadwick et al., 1999), fertiliser use (Brown et al., 2001; Ma et al., 2010) or secondary emissions caused by leaching losses from soils (Reay et al., 2009). Lesser quantified sources of $N_2O$ such as ditches, gateways and feeding troughs are also potentially large emitters (Cowan et al., 2015; Matthews et al., 2010), but are not always accounted for in current $N_2O$ inventories due to a lack of available measurement data. In order to effectively manage and mitigate agricultural emissions of $N_2O$ it is important to understand both the magnitude of emissions from different sources at the farm scale and to identify the most significant drivers of variation in $N_2O$ flux between these sources. Better identification and quantification of high $N_2O$ flux sources may increase our ability to mitigate farm scale emissions by identifying simple farm management practices that have a positive impact.

The vast majority of studies into agricultural sources of $N_2O$ have used chamber methodology to measure fluxes. These measurements typically show a highly skewed, approximately log-normal distribution, with a small number of very high values (Cowan et al., 2015: Folorunso and Rolston, 1984; Velthof et al., 1996; Yanai et al., 2003). To infer the total flux from a whole field (i.e. the population of interest which has been sampled), the integral of the estimated log-normal distribution over the field is simply given by the mean flux ($\mu$) multiplied by the area of the field. However, $\mu$ is poorly estimated by the arithmetic mean of the samples, because of its sensitivity to outliers. $\mu$ is therefore often highly uncertain, but estimating the uncertainty in the arithmetic mean of log-normally distributed data is problematic (Land, 1972). The density of a log-normally-distributed variate, $x$, is given by:

$$d = 1/\left(\sqrt{(2\pi)}\,\sigma_{log}x\right) exp(-((log(x) - \mu_{log})^2/\,(2\sigma_{log}^2))) \quad (1)$$

where $\mu_{\mathrm{log}}$ and $\sigma_{\mathrm{log}}$ are the mean and standard deviation of the log-transformed variate. The mean of the distribution (i.e. without log transformation) is given by:

$$\mu = \exp(\mu_{log} + 0.5\sigma_{log}^2) \quad (2)$$

Estimates of the parameters of the underlying log-normal distribution, $\mu_{\mathrm{log}}$ and $\sigma_{\mathrm{log}}$ (and thereby the true value of $\mu$), are often poor because of small sample size, measurement error and large variability. In order to better predict fluxes at the field or farm scale we therefore need a sound method for quantifying the uncertainty in $\mu$ which arises in estimating whole-field-scale fluxes from a small, log-normally distributed sample. Several methods have been proposed previously for calculating confidence intervals for the mean of a log-normally distributed variable (El- Shaarawi and Lin, 2007; Land, 1972; Parkin et al., 1990). However, with small sample sizes and/or large variability, these methods are often unsatisfactory, and can result in implausibly large intervals (Zou et al., 2009).

The primary aim of this study was to identify and compare the most significant sources of $N_2O$ emissions from a typical livestock farm in Scotland, with a focus on $N_2O$ emissions from sources which are not associated directly with nitrogen fertiliser application, since the latter are already well-documented. A secondary aim was to examine the chemical properties of the soils in locations from which flux measurements were made in order to explain the variability in $N_2O$ emissions across the wide range of soil environments sampled across the farm. Our third aim was to investigate methods for upscaling point measurements to estimate whole-farm emissions and the associated uncertainties using a Bayesian approach.

## 2. **Materials and methods**

### *2.1. Farm description*

The Easter Bush Farm Estate is a combination of several farms near Penicuik, Midlothian in Central Scotland (55° 51' 55.7036"N, 3° 12' 44.3549"W). These farms are owned by either by Scotland's Rural College (SRUC) or the University of Edinburgh (UoE) and are run for commercial and research purposes. A selection of twenty separate fields where chosen which represented the wide variety of management practices within the estate and which were readily accessible for our flux measurement equipment. These fields covered approximately 133 ha of land and were chosen to represent a typical Scottish livestock farm in this study (Table 1). Fields were either used for growing arable crops for fodder (barley, oilseed rape, or silage grass) or as grazing pasture for sheep or cattle. The farm managers at the estate estimated that the selected fields and sheltered barns would provide for 440 ewes with 835 lambs and 86 cattle with 60 calves over the period of a year. The perimeter and area of each field was measured manually using a handheld GPS device (Garmin eTrex Legend HCx, Garmin, Shaffhausen, Switzerland).

### *2.2. Quantification of $N_2O$ source area coverage*

Using GPS measurements, we estimated the total area coverage of each of the arable and grazed fields each season to within ±10 %. The area coverage of the farm was fairly evenly split between arable and grazing use (Table 2). Some of the larger grass fields were switched between livestock grazing and silage grass (arable) for several months at a time (see Table 1). Cattle were moved between barns and pasture, whereas the sheep spent all year round in the fields. Our measurements covered the general grazed grasslands and arable fields, and several smaller features which we identified as potentially important sources of $N_2O$. These features were areas of the farm which were used more intensively, and comprised: areas around animal feeding and drinking troughs; areas that had recently been used for manure storage; disturbed areas e.g. near gates or recently tilled; manure heaps; the concrete-floored barns which accumulated animal waste; and silage heaps. Calculation of the areas of these features was more uncertain. For example, a single manure heap and surrounding area contaminated by the heap covered an area of 532 $m^2$, but the relative proportions changed seasonally as the heap grew in size (up to 3 m high) and was spread onto arable crops in autumn. The capacity of the bedding area of the animal barns was ~2500 $m^2$, but the area used by the cattle varied seasonally. This was relatively high in the autumn and winter months (60 – 80 %) and lower for the rest of the year (~20 %). The silage heap was approximately 3.5 m tall and covered a total of 300 $m^2$ when full after harvesting in early autumn, but this was progressively reduced over the following year. The uncertainty in the area of these features was estimated to be 50 %, because of the difficulty involved in accurately identifying the true area coverage by visual inspection. Based on these estimates, the features accounted for approximately 0.3 % of the total area of the farm.

### *2.3. Meteorological conditions*

Air temperature and rainfall (tipping bucket) were monitored by a permanent meteorological monitoring station at the farm. The meteorological data recorded from this site is assumed to be representative for the entire farm area throughout the inventory measurement period due to the relatively small distance between the fields and the monitoring station. Annual cumulative rainfall for the period between July 2012 and August 2013 was 962 mm. The average annual rainfall over the past ten years (2001 – 2011) was 921 mm, which suggested that rainfall during the measurement period was fairly typical (Figure 1a). Daily temperatures recorded were considered typical during the year in which measurements took place (Figure 1b).

### *2.4. Dynamic chamber flux measurements*

A high-precision dynamic closed chamber system (Cowan et al., 2014a) was deployed to measure $N_2O$ fluxes during four seasonal measurement periods between autumn 2012 and summer 2013. A pump (SH-110, Varian Inc, CA, USA) circulated air between the flux chamber (7 l min$^{-1}$) and a compact continuous wave quantum cascade laser (QCL) gas analyser (CW-QC-TILDAS-76-CS, Aerodyne Research Inc., Billerica, MA, USA) over a three minute period (as in (Cowan et al., 2014a). The QCL instrument (instrumental noise of 30 ppt at 1 Hz) was secured inside an off-road vehicle to allow mobile measurements, powered by a diesel generator. The chamber (non-transparent, 39 cm$^2$ diameter, height 26 cm and volume 0.03 m$^3$) was placed onto circular stainless steel collars which were inserted 5 cm into the soil several minutes prior to each measurement. Two 30-m lengths of 3/8 inch ID Tygon® tubing were attached to both the inlet of the QCL and the outlet of the pump. This provided a 30 m radius from the vehicle in which the chamber could be placed (Cowan et al., 2015).

A total of 529 flux measurements were made across the farm between autumn 2012 and summer 2013 (Table 3). Measurement locations were chosen at random across the fields which were accessible for the mobile flux measurement system. Wet weather, difficult terrain and availability of the QCL instrument were limiting factors in the number of measurements that were possible during each measurement period and the areas in which measurements could take place. Typically five or more flux measurements were made from different collars in each field, with some fields being investigated in greater detail. Very wet weather during autumn and winter months reduced the number of measurements which could be made.

### *2.5. Soil sampling and analysis*

Two types of soil samples were taken at 457 of the flux chamber measurement locations. Soil samples (5 cm deep) were taken from within the chamber collar using a 2 cm wide corer immediately after a flux measurement was complete. These soils were frozen to - 18 ˚C within six hours of collection until analysis up to two months later. The wet samples were defrosted in a refrigerated room (5 ˚C) overnight prior to analysis of pH (in $H_2O$) and available nitrogen in the form of ammonium ($NH_4^+$) and nitrate ($NO_3^-$). The pH of the soil samples was measured using the method outlined in (Rowell, 1994), p160). Ten grams of air dried soil was placed in a small plastic cup. 20 ml of deionised $H_2O$ was added to the soil and the mixture was shaken and left for 60 minutes. A pH meter (MP220, Mettler Toledo, Columbus, Ohio, USA) was used to measure pH in the soil solution.

Ammonium ($NH_4^+$) and Nitrate ($NO_3^-$) was extracted from the soil samples using KCl extraction as outlined in (Rowell, 1994), p 226). Soil (15 g) was added to a flask and mixed with 50 ml of 1 M KCl solution. The solution was shaken automatically using an orbital shaker for 60 minutes. The mixture was filtered using 2.5 µm filter paper (Fisherbrand, Hampton, New Hampshire, USA) and the solution was stored and frozen in 20 ml plastic vials. Concentrations of $NH_4^+$ and $NO_3^-$ were measured using a Bran and Luebbe AutoAnalyser (SPX Flow Technology, Norderstedt, Germany).

Separate soil samples used to measure bulk density were also taken immediately after the flux measurement using a sharp metal cutting cylinder (7.4 cm diameter, 5 cm deep) which was carefully inserted into undisturbed soil. These soil samples were kept in a refrigerated room (5 ˚C) until oven drying (less than seven days after sample collection). These samples were used to calculate soil moisture content (via oven drying at 100 ˚C) and also provided the dry soil mass. Bulk density was calculated by dividing the volume of the cutting ring by the mass of dry soil. A sub sample of the dried soils was taken to be ground (via ball milling) for elemental analysis of total carbon and nitrogen content of the soil (vario EL cube, Elementar, Hanau, Germany). WFPS was calculated from the bulk density soil samples as described in (Rowell, 1994).

### *2.6. Regression analysis*

The "leaps" package for the freely available statistical software R (R Core Team, 2013 ) was used to perform step-wise regression to find the best-fitting model, based on the Akaike information criterion (AIC) (Lumley, 2015). AIC is a measure of model goodness-of-fit derived from information theory, widely used in model selection (Burnham and Anderson 2004). It is based on the model likelihood, penalised by model complexity, as measured by the number of parameters. For a set of candidate models, the model with the lowest AIC value represents the best choice, given the trade-off between model likelihood and complexity. Using this approach, we selected the model which provided the best fit to the $N_2O$ flux data, given the available explanatory variables.

### *2.7. Statistical analysis and upscaling*

A Bayesian approach (Wild et al., 1996; Zellner, 1971) was applied to constrain the plausible range of the mean $N_2O$ flux. We carried out Markov Chain Monte-Carlo (MCMC) simulations using the freely-available JAGS software (Plummer, 2003) which implements Gibbs sampling to estimate the posterior distribution of $\mu$, by combining the prior with the data. We used an informative prior in the form of a log-normal distribution, with mean and variance based on the $N_2O$ fluxes predicted by the regression analysis described above. For each field/feature, we derived the relationship between $N_2O$ flux and soil nitrogen based on data from all the other fields/features, and used this to predict the expected distribution of $N_2O$ flux in the field/feature of interest. This allowed us to incorporate our knowledge of this functional relationship into our prior expectation of the $\mu_{\log}$ and $\sigma_{\log}$ parameters. Generally, the data dominate the posterior distribution, except where the data do not show a clear log-normal distribution, and so do not strongly constrain the fit of the $\mu_{\log}$ and $\sigma_{\log}$ parameters. Here, the prior acts to constrain values of $\mu$ to within the range expected, given the relationship with soil nitrogen, and thereby down-weights implausibly high values of $\mu$. We did this for each of the source categories in Table 3 to estimate $\mu$, with 95 % confidence intervals from the quantiles of the posterior distribution. For comparison, we also calculated the naïve sample mean and confidence intervals (i.e. based solely on the sample data), and also using the method outlined in (Zou et al., 2009) as implemented in the EnvStats package for R (Millard, 2016).

In our data set, fluxes varied unpredictably by five orders of magnitude over short distances (<10 m), within all the features we identified and by four orders of magnitude for the general fields. We examined semivariograms for the $N_2O$ fluxes and ancilliary data, in which the semi-variance is plotted as a function of distance between spatial points, using the GeoR package in R (Ribeiro, 2016). These showed no evidence of spatial autocorrelation in the data at any scale. Classical geostatistical interpolation methods, such as Kriging, were therefore not applicable in spatial upscaling, and the whole field or feature-scale emission can be estimated as $\mu$ multiplied by the field/feature area. In each season, the whole-farm emission estimates were calculated by summing the emissions from all of the source categories. Uncertainty in the mean flux was propagated with the uncertainty in the area of each source category by adding variances to provide the uncertainty in the whole-farm emission. Due to the lack of measurements made in winter, we estimated emissions from sheep-grazed fields based on a combination of both the arable and cattle fields during the same period.

## 3. Results

### 3.1. $N_2O$ flux measurements

Individual $N_2O$ flux measurements varied by five orders of magnitude, with values between -5.5 and 352,900 µg $N_2O$-N $m^{-2}$ $h^{-1}$ (Figure 2). The log-normal distribution of the fluxes in the differently managed general field types is fairly consistent across the farm (as observed in Figure 2). Fluxes from the features appeared to follow a log-normal distribution, varying by up to five orders of magnitude. Fluxes measured from disturbed soils varied in magnitude similar to the measurements on the general areas in the same fields, but also included some very high fluxes (> 10,000 µg $N_2O$-N $m^{-2}$ $h^{-1}$). Fluxes measured from manure in the animal barns and outdoor manure heaps were very variable, between 1 and 80,000 µg $N_2O$-N $m^{-2}$ $h^{-1}$ and most were considerably higher than those measured from the general field areas. We measured fluxes from the base of the manure heaps to the top (up to 3 m high) and no relationship was observed between $N_2O$ flux and height of the manure heaps. Fluxes measured from the stored silage grass at the farm also varied by five orders of magnitude. The single largest flux measurement recorded from the entire farm area was from a decaying clump of wet grass at the bottom of the silage heap in summer. This small pile of grass had begun to turn black and was coated with fungi. A single extreme flux of 352,900 µg $N_2O$-N $m^{-2}$ $h^{-1}$ was recorded from this small patch (approximately 40 $cm^2$ in size) of decomposing silage grass which had collected on a concrete surface for several weeks or months. This measurement was excluded from the silage heap grouping as it was considered an oddity and not representative of the remaining grass in the heap.

### 3.2. Summary of all soil measurements

Soil temperatures during flux measurement periods reached a minimum of 2 ℃ in winter and a maximum of 19 ℃ in summer (Table 4). Soil temperatures recorded in spring and autumn were similar (approximately 11 ℃). WFPS was generally higher in autumn and winter than it was in spring and summer, although this varied on a case to case basis due to topography, soil type and the varying condition of the field drainage systems present at measurement locations. Average pH values were fairly consistent across the fields in all seasons (~ 6.4), although several individual measurements varied widely from this value (Figure 3). Bulk density varied across the farm with a maximum of 1.6 g $cm^{-3}$, a minimum of 0.4 g $cm^{-3}$ and an average value of 0.9 g $cm^{-3}$. Individual measurements of total carbon and total nitrogen content of the soils across the farm varied widely from all sources; however, no patterns could be established between the different sources and seasons (Table 4).

A seasonal variation was observed in concentrations of available nitrogen ($NH_4^+$ & $NO_3^-$) measured from the general fields (Table 4). Available nitrogen concentrations were larger in all field types in spring and summer than in winter and autumn. The log-normal distribution of both $NH_4^+$ & $NO_3^-$ concentrations (Figure 4) were similar to that of the $N_2O$ flux measurements (Figure 2). Like $N_2O$ fluxes, the individual available nitrogen measurements also varied unpredictably by several orders of magnitude over short distances (< 10 m). Available nitrogen concentrations were considerably higher in the feeding area and manure contaminated soils than they were in the general areas on the fields (Table 4).

### *3.3. Relation between soil properties and $N_2O$ flux*

The correlations between individual $N_2O$ fluxes and soil properties are fairly poor (Figure 4). The strongest correlation is observed between log(Flux) and log($NO_3^-$), accounting for 41% in the variance of individual measurements ($n$ = 449). Grouping measurements that were taken from the same field/source on the same day improves the correlation between flux and soil properties. The strongest correlation observed using this grouping is also between log(Flux) and log($NO_3^-$) with 71 points explaining 62 % of the variance. When grouping the data based on each of the emission sources by the season in which they were measured (as in Table 4) the relationship correlates strongest between log(Flux) and either $NO_3^-$ or log($NH_4^+$), both with relatively high $R^2$ values of 0.86. In each of the groupings it is clear that $N_2O$ flux correlates considerably better with the soil available nitrogen ($NH_4^+$ and $NO_3^-$) than with any of the other properties for which the univariate correlations are relatively weak in this data set.

Using best-subsets regression, we select the model which best explains the variability in $N_2O$ fluxes, based on the lowest AIC value (Table 5). For the individual chamber measurements univariate linear regression between log(Flux) and log($NO_3^-$) results in the lowest AIC value. The AIC analysis suggests that adding further information does not significantly improve this, although a higher $R^2$ value is possible using more variables (See Table 5). Multivariate regression of the data grouped by the field proximity and date provides a better fit than that of the individual measurements (Table 5 and Figure 5) accounting for 66 % of the variance, although this is only increased slightly from the variance of 62 % accounted for when using univariate linear regression with either $NO_3^-$ or log($NH_4^+$)). Multivariate regression accounts for up to 91 % of the variance in the data grouped by source type and season; however, this fit is heavily influenced by only 3 points with high associated available nitrogen and $N_2O$ flux measurements (i.e. manure contaminated soils) ($R^2$ = 0.76 without these points) (See Figure 5).

### *3.4. $N_2O$ flux measurements at the farm scale*

Mean fluxes measured from the feature areas were considerably higher than those measured from the general field areas, by about two or three orders of magnitude (Table 6). However, the general field areas contributed more to the whole-farm emissions than the feature areas (Table 7), due to their large area occupying around 99.7 % of the farm. Seasonal differences were observed in fluxes from the general field areas, with the highest values observed in spring and summer (Table 6). This same pattern was reflected in the farm-scale flux estimates (Table 7). In the spring and summer, the general field areas contributed 77 to 93 % of the whole-farm emission (depending on statistical method, Table 7). In winter, fluxes from the general field areas were very low, and the feature areas dominated the whole-farm-scale emission, contributing between 74 to 91 % of the total (Table 7).

The naïve sample mean tended to be higher than the Bayesian or Zou et al., 2009 methods when high values occurred in the sample, and were lower in data sets without large outliers. The naïve sample confidence intervals are symmetrical, and the lower limit was often negative (and probably erroneous) and the upper limit was often implausibly large. The Bayesian and or Zou et al., 2009 methods provided plausible, asymmetric confidence intervals, which were often similar. When sample size was small or variability very large, the method of Zou et al., 2009 produced very high upper limits, sometimes several orders of magnitude too high (Table 7), and these have to be considered implausible, given the data. The Bayesian method was robust, giving plausible confidence intervals in all cases, and is the preferred method, despite the slightly greater computation time and complexity. Where a log-normal distribution is not well-defined by the data (such as for the feature areas), the Bayesian method tends to estimate a lower mean than the method of Zou et al., 2009, which is a consequence of the prior we used.

## 4. Discussion

### 4.1. $N_2O$ fluxes at the farm scale

This study highlights the variability of $N_2O$ fluxes present at the farm scale and the difficulties involved in upscaling these measurements. Individual flux measurements ranging from -5.5 to as large as 80,000 µg $N_2O$-N $m^{-2}$ $h^{-1}$ were recorded from various sources present at the farm; however a large proportion of the measured fluxes were close to zero. The detection limit of the dynamic chamber method used is estimated to be 4 µg $N_2O$-N $m^{-2}$ $h^{-1}$ (Cowan et al., 2014a). As 20 % of the fluxes measured at the farm scale were lower than this detection limit, it is likely that the large proportion (11 %) of negative fluxes recorded during the study are a result of the detection limit of the instrumentation rather than the measurement of true negative fluxes (Cowan et al., 2014b). This highlights the need for flux measurement methodology with low detection limits for detailed investigation of $N_2O$ fluxes and relationships between emissions and the soil properties which drive microbial processes in agricultural soils.

The largest $N_2O$ fluxes per unit area observed were generally measured from the feeding areas, manure-contaminated areas, animal barns and manure heaps. These fluxes can be attributed to the higher concentration of available nitrogen from animal waste deposited to these areas. The farm-scale contribution to fluxes from these sources is difficult to estimate for two reasons. Firstly, difficulties remain in accurately identifying (or defining) the area occupied by these features. In this study, stratification of the farm area was achieved using a mixture of GPS measurements and some assumptions to estimate the areas of each of the feature areas. However, this method grossly generalises these features which in reality, may be considerably different between different fields under different management. Each area of the farm would require numerous flux and soil measurements to properly define it, which becomes impractical at increasingly large scales. It is also possible that further areas exist within the grazing fields in which animal waste deposition (and therefore available nitrogen) is significantly higher than the general field coverage such as ditches, riparian areas and shaded or dryer areas which are not accounted for in this study (Cowan et al., 2015; Groffman et al., 2000; Matthews et al., 2010). The second difficulty is that spatial variability from these sources is large, resulting in very large uncertainties when upscaling. The direct log relationship between $N_2O$ flux and available nitrogen explains in part why these very large fluxes occur; however, it does little to help improve up-scaling estimates as spatial variability in available nitrogen is just as unpredictable as that of $N_2O$ and is also more expensive to measure. The results in this study suggest that although flux contributions from these low area coverage high flux sources are smaller than the contribution from the general field areas, they are still significant enough to include in large scale (farm to regional) $N_2O$ inventories. It is also worth considering that, as each farm is unique in terms of size and management, the contributions from these sources are likely to vary considerably on a farm to farm basis.

Fluxes measured from the general areas on the fields in spring and summer were larger than those in autumn and winter. It is likely that these seasonal variations are caused by multiple seasonal variations in soil conditions rather than a single definitive factor, although the only statistically significant correlation observed between the measurements in this study is the relationship between flux and available nitrogen (Figure 5). Measurements were made at times chosen to avoid peaks in fluxes after fertilisation events which tend to occur in a three week period after fertilisation (Skiba et al., 2013; Smith et al., 2012); however, the majority of nitrogen fertilisers used at the farm were applied to the fields in spring and summer and it is likely the elevated available nitrogen measured across the farm in these seasons is partly due to remaining residues of these fertilisers in soils. Higher nitrogen in soils may also be due to animal waste input, especially in the densely stocked sheep fields during the lambing season. It is known that elevated available nitrogen in soils from livestock waste results in larger $N_2O$ fluxes (Gill et al., 2010; Šimek et al., 2006); however, a relationship is sometimes difficult to define in field studies due to the competing effects of numerous other heterogeneous soil properties, especially WFPS, which influence fluxes in a less discernible manner. Other studies have also observed seasonal variation in $N_2O$ fluxes from animal waste, but relationships between nitrogen deposition and fluxes reported in these publications are inconsistent with our observations (Allen et al., 1996; Wolf et al., 2010).

### *4.2. Spatial interpolation of $N_2O$ flux measurements*

Upscaling chamber fluxes spatially has proven difficult in many studies (Folorunso and Rolston, 1984; Hénault et al., 2012; Velthof et al., 1996). Variation in $N_2O$ flux measurements observed in this study was as similar at small distances (< 10 m) as it was at large distances (> 100 m) from all sources. This is a common phenomenon when measuring $N_2O$ with flux chambers (Ball et al., 1997; Hargreaves et al., 2015). Without a spatial pattern the use of interpolation methods such as kriging and regression models are limited. In this study no statistically significant variance could be identified between flux measurements at any scale, although a consistent and randomly spaced log-normal distribution of measured flux magnitude was observed across all sources of $N_2O$ at the farm. The observation of log-normal distributions in $N_2O$ flux measurements is very common from agricultural soils (Folorunso and Rolston, 1984; Velthof et al., 1996; Yanai et al., 2003).

The log-normal nature of $N_2O$ flux measurements makes up-scaling fluxes uncertain. Using the naive sample mean can result in poor flux estimates because of its sensitivity to outliers. Zou's method generally gave results similar to the Bayesian method, but in some cases the uncertainties were implausibly large, when sample size was small and fluxes were high. The Bayesian method allows us to account for the log-normal distribution of the data and propagate the associated uncertainty appropriately to the farm scale. In terms of systematic bias between the methods, there were some differences that were consistent with theory. The naive sample mean is an unbiased estimator in the statistical sense, meaning that with a large enough sample size, it will not deviate systematically from the population mean. However, it is recognised that it is an inefficient estimator of the population mean, meaning that it requires a large sample to be accurate. With small sample sizes and large variance (as is normal with flux data), it will typically underestimate the population mean (because infrequent, high values will often be missing from the sample). When high values are perchance included in the sample, it will typically overestimate the population mean. Here, we explicitly attempt to incorporate high values in our sampling, by focusing on hot spots and point sources, usually ignored in field surveys. Hence, the naive method often produces overestimates in these data sets, compared to the other methods which account for the lognormal distribution. We note that this is atypical, and that underestimation by the naive sample mean will be the more common problem.

The use of methods which cover larger areas when measuring fluxes such as eddy covariance may provide better spatially and temporally integrated data sets for individual fields. Potentially, top-down approaches such as the use of tall towers to measure gas fluxes in the future may improve regional flux inventories without the need for multiple bottom up studies (Baldocchi, 2014; Zhang et al., 2014).

The interpolation of $N_2O$ fluxes using measured soil properties and meteorological data either spatially or temporally is one potential way to up-scale fluxes to the farm scale (i.e. using the relationship between $N_2O$ flux and available nitrogen which explains much of the variability in the observations in this study), but many hurdles remain. Empirical relationships between $N_2O$ flux and soil properties have been reported in the past, each with unique values that best fit their particular data set and measurement conditions (Flechard et al., 2007; Schmidt et al., 2000). The spatial variability of available nitrogen in the soils at the field scale is also similar to that of $N_2O$ and a large amount of additional (and prohibitively expensive) soil nitrogen measurements would be required to improve flux estimates using any predicted relationship.

The WFPS value at which $N_2O$ fluxes peaked in in this study is 38 %. This value is considerably lower than the maximum values reported in other studies which tend to range from 60 to 90 % (Clayton et al., 1997; Flechard et al., 2007; Schmidt et al., 2000). The relatively low value in WFPS in which fluxes peak in this study is more likely to be an artefact of seasonal changes in available nitrogen in the soil than any effect that the WFPS may have on fluxes. Due to the seasonal differences in available nitrogen in this study it is difficult to separate the effects of environmental change on $N_2O$ and effects of the additional nitrogen present in the warmer and drier periods of spring and summer.

## 5. Conclusions

The most significant driver of $N_2O$ fluxes in this study was nitrogen in the form of $NH_4^+$ and $NO_3^-$. Available nitrogen in soils can be as spatially variable as $N_2O$ flux over small and large scales, and it is likely this heterogeneous nature is a significant factor in the spatially unpredictable log-normal distribution of flux measurements. The use of Bayesian methods can improve estimates of upscaled fluxes and their associated uncertainties when the underlying data are log-normally distributed. $N_2O$ fluxes measured from features such as animal feeding troughs, manure heaps and animal barns were typically one to four orders of magnitude higher than those measured from the rest of the farm. However, these sources were typically found to contribute less $N_2O$ at the farm scale when compared to the extensive arable and pasture fields (which covered 99.7 % of the area). The small contribution from the features can sometimes be significant at the farm scale, as potentially up to 91 % of the fluxes may come from only 0.3 % of the area coverage in some cases, and large uncertainties persist in these calculations.

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**Figure 1** (a) Cumulative annual rainfall and (b) daily average temperature were plotted for the years 2001 – 2013 (each line representing a different year) at the Easter Bush Farm Estate. The measurement period of the study is represented with a solid black line in both figures (Jan – Aug 2013 and Sep – Dec 2012).

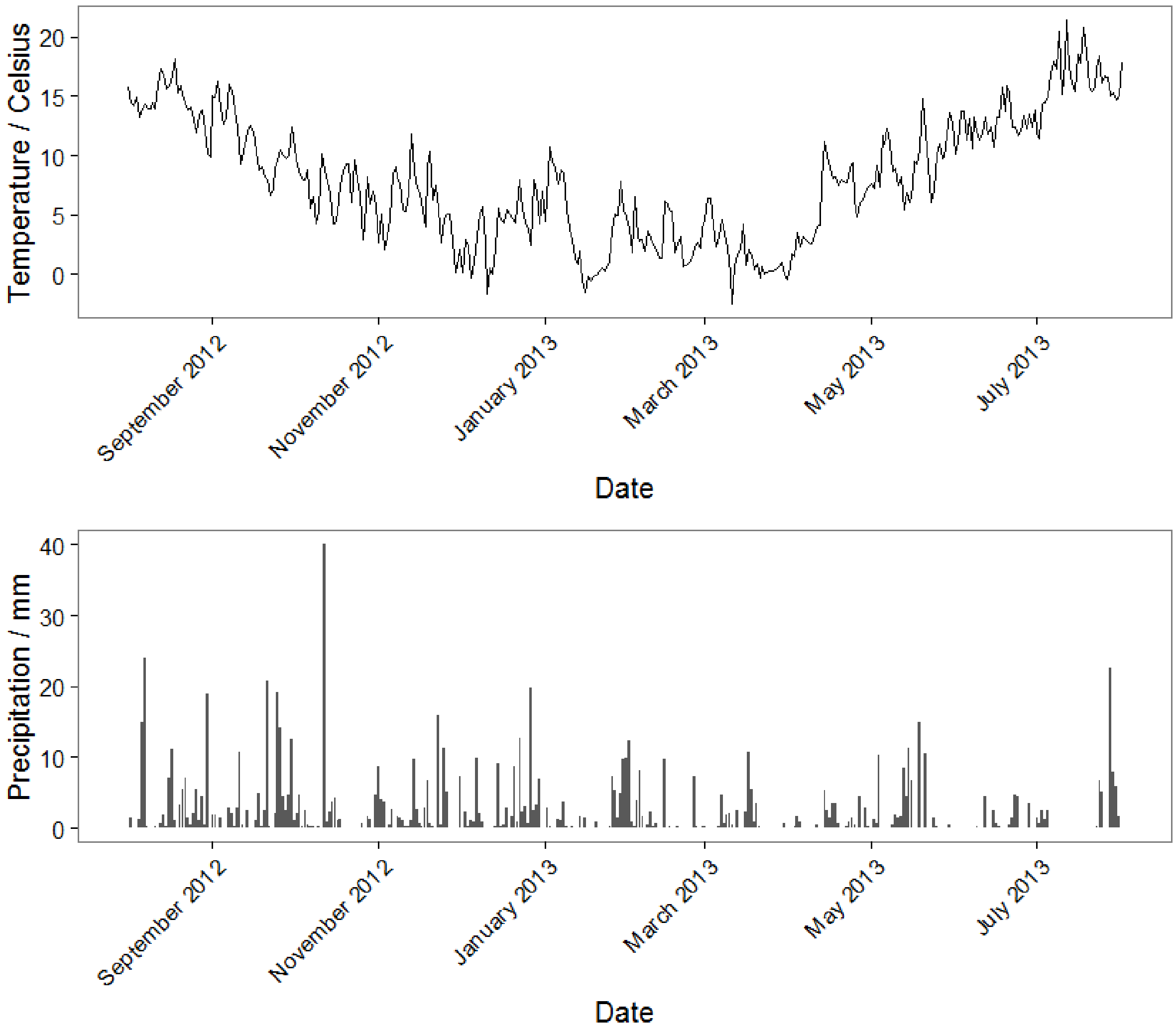

**Figure 2** Frequency distribution of observed $N_2O$ fluxes from the different sources at the farm, shown on a log transformed axis. Measurements representing areas of general field coverage are separated based on management (top). Six sources of features are separated. Negative fluxes are shown on the positive scale but coloured white.

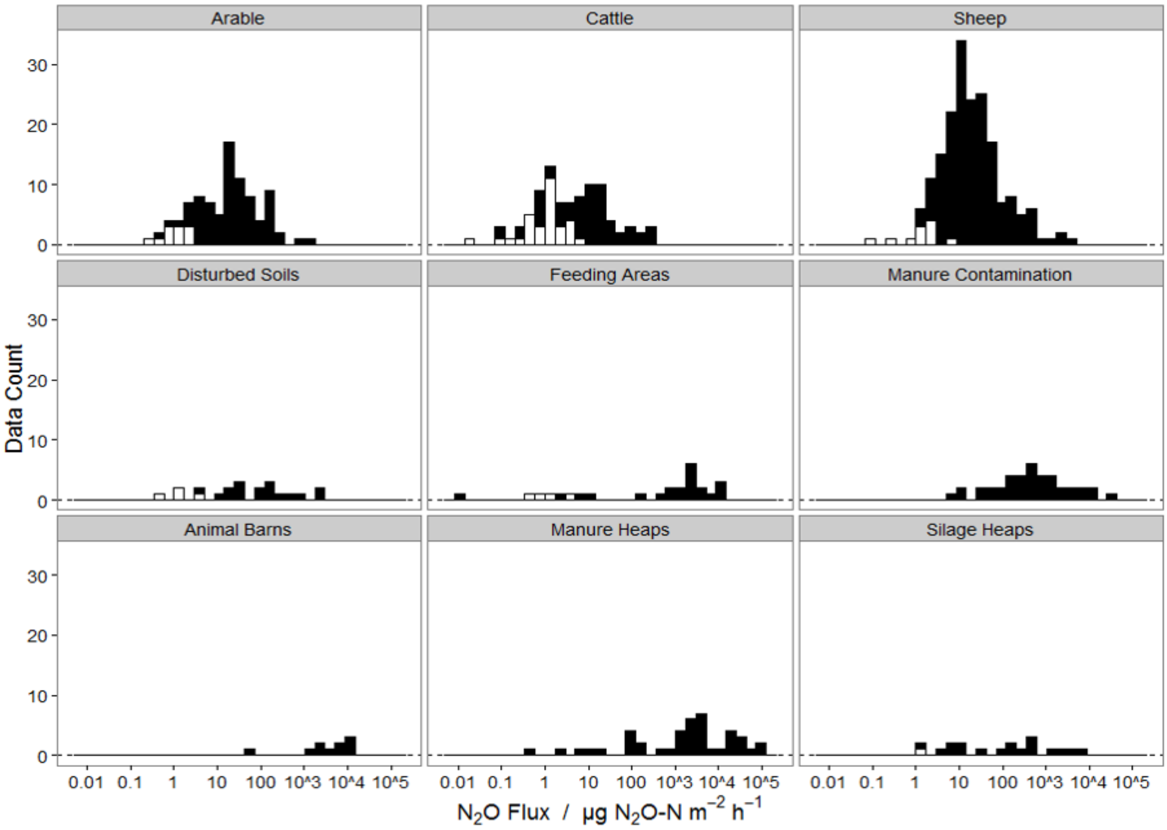

**Figure 3** Frequency distribution of all soil measurements made on the farm. The physical properties (temperature, WFPS and bulk density) of the soil followed a normal distribution, while the nitrogen and carbon content measurements are better described as a log-normal distribution.

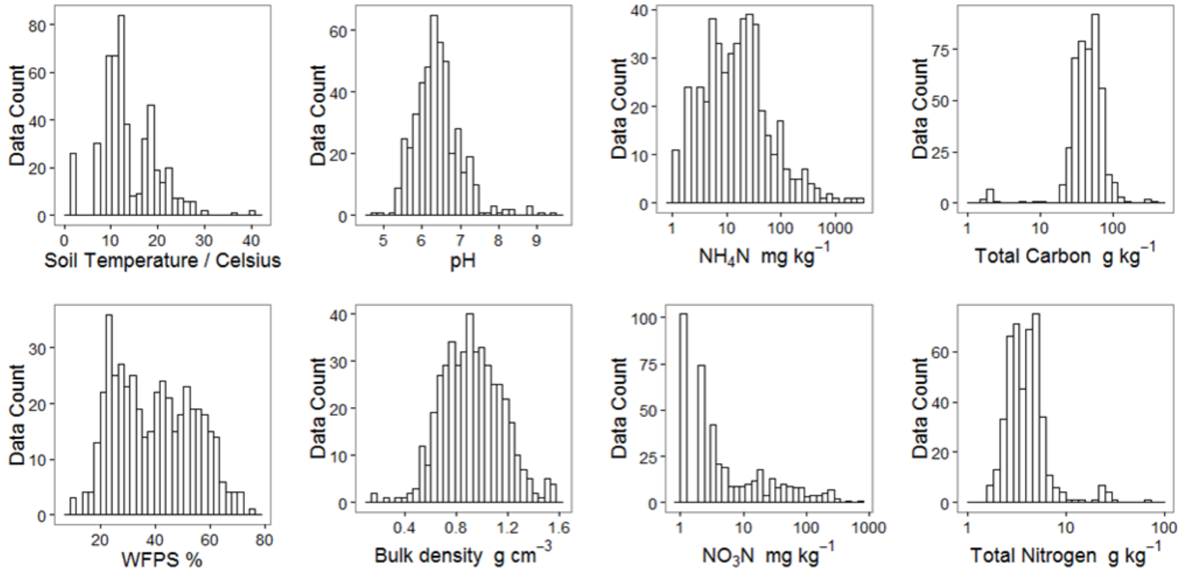

**Figure 4** Percentage of variance in log($N_2O$ flux) explained by univariate linear regression with soil properties (see Table 4 for units).

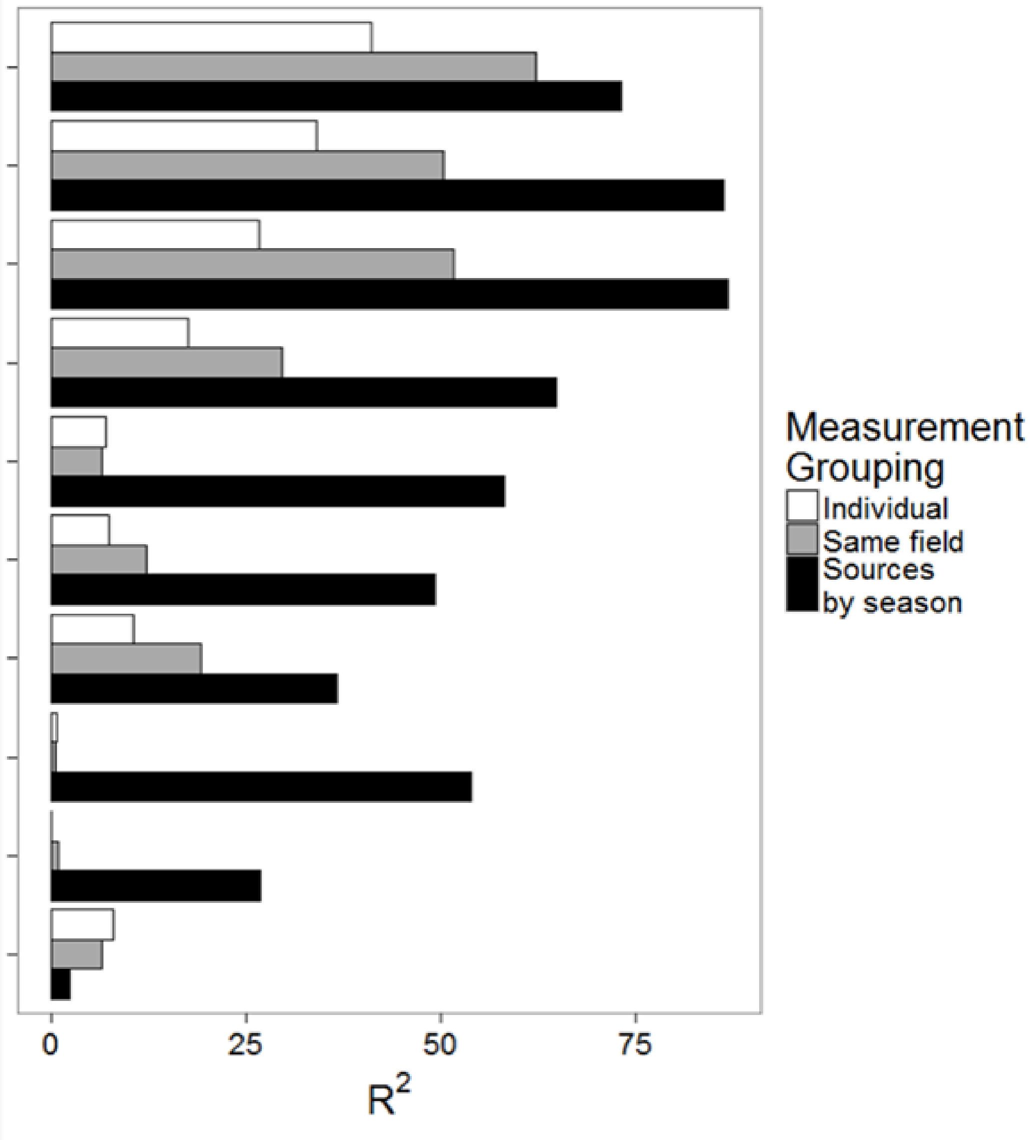

**Figure 5** Measured $N_2O$ flux is plotted against fitted flux based on the best sub-sets regression model with the lowest AIC value (See Table 5). The model fit between $N_2O$ flux and soil properties for (I) individual measurements, (II) measurements made from the same field and date and (III) measurements made from the same source type and season. A 1:1 line is added to each plot.

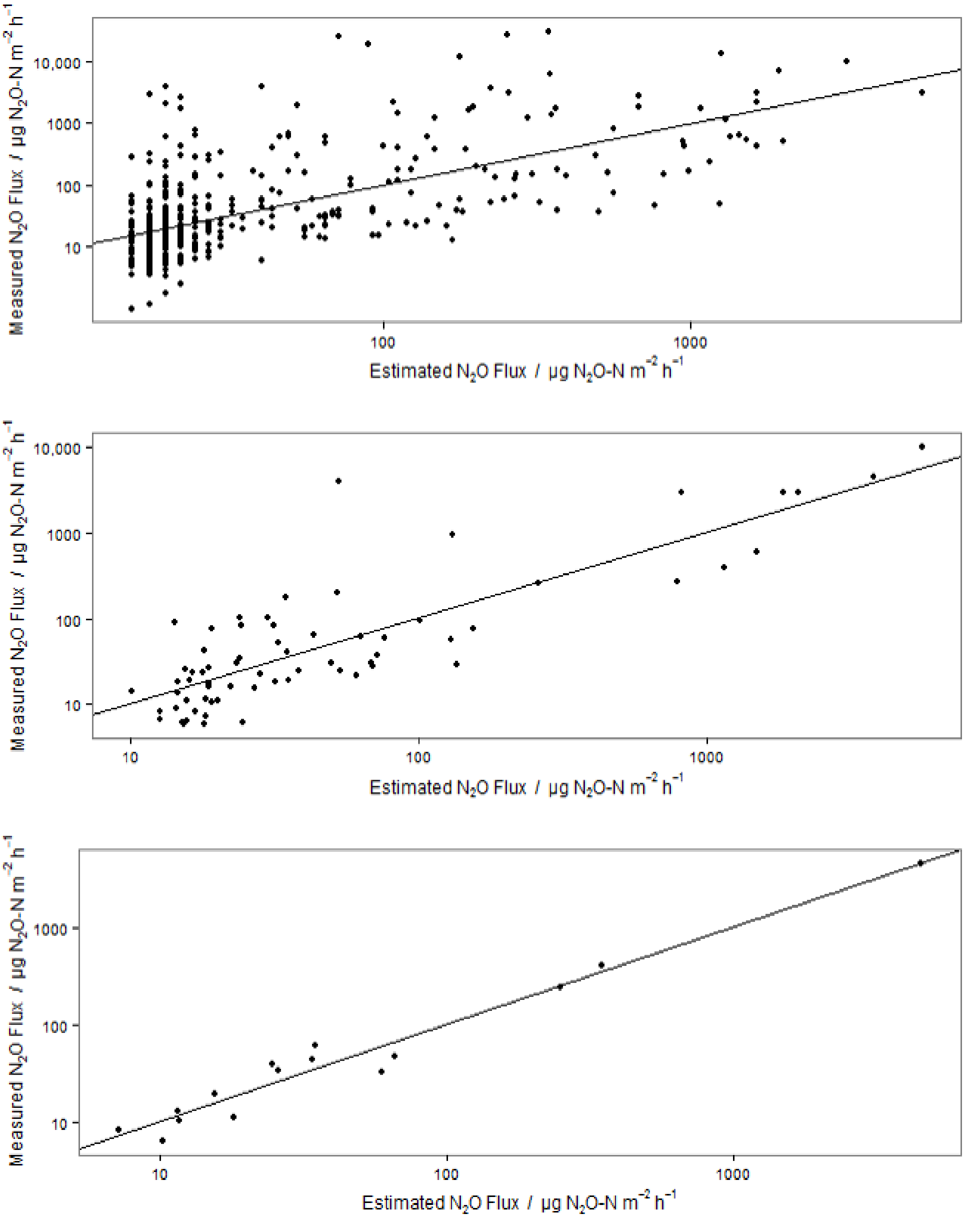

**Table 1** A description of seasonal management of the each of the fields selected to represent the livestock farm in this study.

| Field Name | Area (ha) | Autumn 2012 | Winter 2012/2013 | Spring 2013 | Summer 2013 |
|---|---|---|---|---|---|
| Corner Field | 6.72 | Sheep | Sheep | Sheep | Sheep |
| Engineers Field | 5.30 | Sheep | Sheep | Sheep | Sheep |
| Middle Field | 5.44 | Cattle | Sheep | Sheep | Sheep |
| Paddock Field | 4.08 | Sheep | Sheep | Sheep | Sheep |
| Bog Hall Field | 7.55 | Barley | Empty | Barley | Barley |
| Kimming Hill | 12.16 | Silage | Sheep | Silage | Silage |
| Anchordales | 2.67 | Barley | Empty | Barley | Barley |
| Anchordales N.L.T | 5.36 | Barley | Empty | Barley | Barley |
| Cow Loan | 4.79 | Barley | Empty | Barley | Barley |
| Hay Knowes | 10.92 | Barley | Oilseed | Oilseed | Barley |
| Crofts | 8.67 | Barley | Empty | Barley | Barley |
| Low Fulford | 7.72 | Silage | Sheep | Silage | Silage |
| Fulford Camp | 5.37 | Sheep | Sheep | Sheep | Sheep |
| Mid Fulford | 9.57 | Cattle | Empty | Sheep | Sheep |
| Fulford Stackyard | 3.68 | Sheep | Sheep | Sheep | Sheep |
| Upper Fulford | 4.48 | Sheep | Empty | Cattle | Cattle |
| Nuek | 4.89 | Cattle | Empty | Cattle | Cattle |
| Doo Brae | 5.76 | Sheep | Sheep | Cattle | Cattle |
| Woodhouselee Camp | 4.94 | Cattle | Cattle | Cattle | Cattle |
| Lower Terrace | 12.56 | Barley | Empty | Empty | Sheep |

**Table 2** Estimated area of each of the identified source categories. Areas change seasonally due to alternating use of fields (see Table 1)

| Source Category | Autumn 2012 | Winter 2012/2013 | Spring 2013 | Summer 2013 |
|---|---|---|---|---|
| General fields (ha) | | | | |
| Arable | 60.2 ± 6.0 | 52.5 ± 5.3 | 77.8 ± 7.8 | 65.2 ± 6.5 |
| Cattle | 24.8 ± 2.5 | 14.3 ± 1.4 | 20.1 ± 2.0 | 20.1 ± 2.0 |
| Sheep | 47.6 ± 4.8 | 65.8 ± 6.6 | 34.8 ± 3.5 | 47.4 ± 4.7 |
| | | | | |
| Features ($m^2$) | | | | |
| Feeding Areas | 520 ± 260 | 420 ± 210 | 520 ± 260 | 560 ± 280 |
| Disturbed Soils | 1061 ± 503 | 1061 ± 503 | 1061 ± 503 | 1061 ± 503 |
| Manure Contamination | 502 ± 251 | 322 ± 161 | 182 ± 91 | 122 ± 61 |
| | | | | |
| Manure Heaps | 30 ± 15 | 210 ± 105 | 350 ± 175 | 410 ± 205 |
| Animal Barns | 1500 ± 750 | 2000 ± 1000 | 500 ± 250 | 500 ± 250 |
| Silage Heaps | 280 ± 140 | 160 ± 80 | 80 ± 40 | 40 ± 20 |

**Table 3** Number of $N_2O$ flux measurements made from each source category during the study period

| Source Category | All | Autumn 2012[a] | Winter 2012/2013[b] | Spring 2013[c] | Summer 2013[d] |
|---|---|---|---|---|---|
| General field areas | | | | | |
| Arable | 97 | 19 | 18 | 24 | 36 |
| Grassland – cattle-grazed | 92 | 23 | 29 | 29 | 11 |
| Grassland – sheep-grazed | 192 | 26 | 0 | 54 | 112 |
| Features | | | | | |
| Disturbed Soils | 15 | 6 | 6 | 0 | 3 |
| Grassland – feeding areas | 21 | 6 | 1 | 0 | 14 |
| Grassland – manure contaminated | 40 | 0 | 2 | 20 | 18 |
| Animal Barn | 10 | 0 | 0 | 0 | 10 |
| Manure Heaps | 42 | 11 | 5 | 6 | 20 |
| Silage Heaps | 20 | 0 | 0 | 10 | 10 |

[a] 24/09/12 - 28/09/12, [b] 12/02/2013 - 14/02/2013, [c] 03/05/2013 - 16/05/2013, [d] 02/07/2013 - 10/07/2013

**Table 4** Averaged values for each of the measured soil properties in the different source categories each season.

| Source categories | Season | Soil T (˚C ) | WFPS (%) | pH | Bulk Density (g $cm^{-3}$) | $NH_4$-N (mg $kg^{-1}$) | $NO_3$-N (mg $kg^{-1}$) | Total Carbon (g $kg^{-1}$) | Total Nitrogen (g $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| Arable | Autumn | 12.3 | 60 | 6.4 | 1.3 | 3.0 | 1.2 | 42 | 3.0 |
| Arable | Winter | 2.0 | 49 | 6.3 | 1.1 | 3.7 | 3.6 | 30 | 2.5 |
| Arable | Spring | 12.1 | 29 | 6.5 | 1.0 | 23.6 | 22.0 | 34 | 2.9 |
| Arable | Summer | 17.6 | 26 | 6.7 | 1.1 | 23.8 | 18.6 | 24 | 8.5 |
| Cattle | Autumn | 10.6 | 49 | 6.4 | 0.9 | 14.8 | 2.0 | 53 | 4.2 |
| Cattle | Winter | 7.0 | 52 | 6.5 | 0.9 | 8.6 | 1.6 | 52 | 4.2 |
| Cattle | Spring | 10.3 | 47 | 6.1 | 0.8 | 23.7 | 5.4 | 57 | 4.7 |
| Cattle | Summer | 18.3 | 26 | 6.3 | 0.8 | 15.6 | 2.0 | 62 | 4.6 |
| Sheep | Autumn | 11.0 | 55 | 6.2 | 1.0 | 12.3 | 1.3 | 34 | 3.3 |
| Sheep | Winter | NA | NA | NA | NA | NA | NA | NA | NA |
| Sheep | Spring | 10.6 | 47 | 6.3 | 0.9 | 20.9 | 4.8 | 47 | 4.1 |
| Sheep | Summer | 18.8 | 27 | 6.1 | 0.8 | 51.9 | 24.1 | 57 | 4.6 |
| Feeding Areas | All* | 17.0 | 44 | 6.5 | 1.0 | 166.5 | 77.5 | 58 | 4.6 |
| Disturbed Soils | All* | 9.3 | 43 | 6.4 | 1.0 | 21.0 | 11.7 | 36 | 6.7 |
| Manure Cont. | All* | 12.8 | 36 | 6.8 | 1.0 | 117.8 | 90.4 | 47 | 3.9 |

* All measurements for the yearlong study are combined into one group

**Table 5** Results of best sub-sets regression on log($N_2O$ flux), which identifies the best combination of variables for each grouping of data in the data sets. Models with the lowest AIC value are considered most suitable by the analysis.

| Terms | Adjusted $R^2$ | AIC |
|---|---|---|
| **Individual Measurements, n = 449** | | |
| Log $NO_3$-N | 0.41 | 210 |
| Log $NO_3$-N + Log $NH_4$-N + $NO_3$-N + $NH_4$-N + pH + Soil C + Soil T + Bulk Dens | 0.49 | 240 |
| Log $NO_3$-N + Log $NH_4$-N + $NH_4$-N + pH + Soil C + Soil N + Bulk Dens + WFPS % | 0.48 | 240 |
| Log $NO_3$-N + Log $NH_4$-N + $NH_4$-N + pH + Soil C + Soil N + WFPS % | 0.48 | 250 |
| | | |
| **Grouped by field proximity, n = 71** | | |
| Log $NO_3$-N + Log $NH_4$-N + $NO_3$-N + $NH_4$-N + pH + Soil C + Soil N + Bulk Dens | 0.66 | -44 |
| Log $NO_3$-N + Log $NH_4$-N + $NO_3$-N + $NH_4$-N + pH + Soil N + Bulk Dens | 0.66 | -48 |
| Log $NO_3$-N + Log $NH_4$-N + $NO_3$-N + $NH_4$-N + pH + Soil N | 0.67 | -52 |
| Log $NO_3$-N + Log $NH_4$-N + $NO_3$-N + $NH_4$-N + Soil N | 0.67 | -56 |
| | | |
| **Sources by season, n = 15** | | |
| Log $NH_4$-N + $NO_3$-N + pH + Soil C + Soil N + Soil T + Bulk Dens + WFPS % | 0.9 | -23 |
| Log $NH_4$-N + $NO_3$-N + pH + Soil C + Soil N + Soil T + WFPS % | 0.91 | -26 |
| $NO_3$-N | 0.87 | -26 |
| Log $NO_3$-N + Log $NH_4$-N + $NO_3$-N + Soil C + Soil N | 0.91 | -27 |

**Table 6** Mean $N_2O$ flux values with 95 % C.I.'s estimated for each source category per season using three different methods of calculation (units in µg $N_2O$-N $m^{-2}$ $h^{-1}$).

| | | | Naive Method | 95 % C.I. | | Bayesian Method | 95 % C.I. | | Zou's Method | 95 % C.I. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Source categories | Season | n | Mean Flux | Lower | Upper | Mean Flux | Lower | Upper | Mean Flux | Lower | Upper |
| Arable | Autumn | 19 | **6** | -25 | 36 | **3** | 0 | 6 | **4** | 1 | 18 |
| | Winter | 18 | **6** | -7 | 19 | **7** | 4 | 13 | **6** | 3 | 10 |
| | Spring | 24 | **64** | -75 | 203 | **65** | 41 | 101 | **63** | 41 | 119 |
| | Summer | 36 | **102** | -326 | 530 | **81** | 51 | 128 | **81** | 52 | 159 |
| Cattle | Autumn | 23 | **99** | -757 | 954 | **11** | 4 | 21 | **23** | 8 | 135 |
| | Winter | 29 | **0** | -4 | 4 | **0** | -1 | 1 | **0** | -1 | 1 |
| | Spring | 29 | **57** | -104 | 217 | **46** | 29 | 72 | **56** | 32 | 132 |
| | Summer | 11 | **14** | 0 | 28 | **14** | 10 | 19 | **14** | 10 | 21 |
| Sheep | Autumn | 26 | **46** | -273 | 365 | **21** | 9 | 42 | **27** | 11 | 128 |
| | Winter | 0 | **NA** | **NA** | **NA** | **NA** | **NA** | **NA** | **NA** | **NA** | **NA** |
| | Spring | 54 | **160** | -770 | 1090 | **60** | 43 | 83 | **99** | 60 | 208 |
| | Summer | 112 | **111** | -752 | 973 | **55** | 41 | 73 | **58** | 42 | 87 |
| Feeding Areas | All* | 15 | **2539** | -5125 | 10204 | **2865** | 764 | 8329 | **13094** | 2703 | $1.8\ 10^7$ |
| Disturbed Soils | All* | 21 | **311** | -990 | 1611 | **212** | 91 | 456 | **319** | 122 | 3773 |
| Manure Cont. | All* | 40 | **1749** | -7731 | 11230 | **1288** | 677 | 2339 | **1499** | 758 | 5585 |
| Manure Heap | All* | 10 | **10828** | -28069 | 49726 | **9848** | 4787 | 18767 | **31233** | 11101 | 374048 |
| Animal Barns | All* | 42 | **5038** | -1945 | 12021 | **9202** | 3221 | 22268 | **7874** | 3067 | 186468 |
| Silage Grass | All* | 20 | **901** | -2760 | 4561 | **527** | 215 | 1143 | **1153** | 361 | 46231 |

* All measurements for the yearlong study are combined into one group

**Table 7** Farm scale $N_2O$ inventories are calculated for each of the four seasonal measurement periods using three statistical methods. Flux contributions are split between extensive arable and grazing fields and the areas of the farm in which specific $N_2O$ flux altering features were present (units in g $N_2O$-N $h^{-1}$).

| Season | Source categories | Naive Method Mean Flux | 95 % C.I. Lower | Upper | Bayesian Method Mean Flux | 95 % C.I. Lower | Upper | Zou's Method Mean Flux | 95 % C.I. Lower | Upper |
|---|---|---|---|---|---|---|---|---|---|---|
| Autumn | Majority fields | 50 | -212 | 312 | 15 | 8 | 25 | 21 | 12 | 77 |
| | Feature areas | 11 | -2 | 24 | 17 | 5 | 38 | 21 | 10 | 9345 |
| | **Total** | **61** | **-201** | **323** | **31** | **18** | **55** | **42** | **28** | **9367** |
| Winter | Majority fields | 5 | -2 | 12 | 6 | 3 | 10 | 3 | 2 | 5 |
| | Feature areas | 14 | -3 | 32 | 22 | 7 | 50 | 29 | 14 | 7566 |
| | **Total** | **19** | **0** | **38** | **29** | **13** | **57** | **32** | **17** | **7569** |
| Spring | Majority fields | 117 | -226 | 460 | 81 | 60 | 111 | 94 | 71 | 155 |
| | Feature areas | 8 | -7 | 23 | 10 | 5 | 18 | 22 | 11 | 9344 |
| | **Total** | **125** | **-218** | **468** | **91** | **70** | **122** | **117** | **91** | **9439** |
| Summer | Majority fields | 122 | -374 | 617 | 82 | 60 | 114 | 83 | 62 | 136 |
| | Feature areas | 9 | -8 | 26 | 11 | 6 | 19 | 25 | 12 | 10063 |
| | **Total** | **130** | **-365** | **626** | **92** | **70** | **126** | **108** | **83** | **10147** |