Spatial variability and hotspots of soil $\text{N}_2\text{O}$ fluxes from intensively grazed grassland

N. J. Cowan$^{1,2}$, P. Norman$^2$, D. Famulari$^1$, P. E. Levy$^1$, D. S. Reay$^2$, and U. M. Skiba$^1$

$^1$Centre of Ecology and Hydrology, Edinburgh, UK
$^2$School of Geosciences, University of Edinburgh, Edinburgh, UK

Correspondence to: N. J. Cowan (nickcowanuk@gmail.com)

Abstract. One hundred $\text{N}_2\text{O}$ flux measurements were made from an area of intensively managed grazed grassland in central Scotland using a high-resolution dynamic chamber method. The field contained a variety of features from which $\text{N}_2\text{O}$ fluxes were measured including a manure heap, patches of decaying grass silage, and areas of increased sheep activity. Individual fluxes varied significantly across the field varying from 2 to 79 000 µg $\text{N}_2\text{O-N}$ m$^{-2}$ h$^{-1}$. Soil samples were collected at 55 locations to investigate relationships between soil properties and $\text{N}_2\text{O}$ flux. Fluxes of $\text{N}_2\text{O}$ correlated strongly with soil $\text{NO}_3^-$ concentrations. Distribution of $\text{NO}_3^-$ and the high spatial variability of $\text{N}_2\text{O}$ flux across the field are shown to be linked to the distribution of waste from grazing animals and the resultant reactive nitrogen compounds in the soil which are made available for microbiological processes. Features within the field such as shaded areas and manure heaps contained significantly higher available nitrogen than the rest of the field. Although these features only represented 1.1 % of the area of the field, they contributed to over 55 % of the total estimated daily $\text{N}_2\text{O}$ flux.

1 Introduction

Nitrous oxide ($\text{N}_2\text{O}$) is the single largest contributor to global stratospheric ozone depletion (Ravishankara et al., 2009) and a potent greenhouse gas (GHG). $\text{N}_2\text{O}$ is formed naturally in soils and aquatic environments, primarily as a by-product of the microbial processes of nitrification and denitrification (e.g. Davidson et al., 2000; Wrage et al., 2001). Agricultural activities such as the use of nitrogen fertilisers and livestock farming have dramatically altered the natural nitrogen cycle in agricultural environments resulting in significantly increased global emissions of $\text{N}_2\text{O}$ since pre-industrial times (IPCC, 2007). Agriculture is believed to be the largest source of global anthropogenic $\text{N}_2\text{O}$ emissions with estimates as high as 80 % of all anthropogenic emissions due directly or indirectly to agricultural activities (Isermann, 1994; IPCC, 2007).

Large-scale $\text{N}_2\text{O}$ flux estimates for terrestrial sources are often subject to large and poorly defined uncertainties which can limit the effectiveness of mitigation efforts in the agricultural sector (e.g. Bouwman et al., 1995; Oenema et al., 2005). Even estimates of $\text{N}_2\text{O}$ fluxes from agricultural sources at much finer scales (i.e. the plot and farm scale) can be highly uncertain. This is predominately caused by the large temporal and spatial variability of $\text{N}_2\text{O}$ fluxes due to the high heterogeneity of soil properties and microbiological processes (Parkin, 1987; Zhu, J. et al., 2013; Chadwick et al., 2014). Soil properties which are believed to increase $\text{N}_2\text{O}$ emissions by influencing the nitrification and denitrification processes include available nitrogen (in the form of ammonium ($\text{NH}_4^+$) and nitrate ($\text{NO}_3^-$)), available organic carbon, oxygen supply and pH (Bateman and Baggs, 2005; Davidson et al., 2000; Although it is known that these properties can alter $\text{N}_2\text{O}$ production in soils, it is still difficult to accurately simulate the net effect on $\text{N}_2\text{O}$ fluxes from areas (that are often considered to be homogeneous land cover) such as agricultural fields used for arable crops and grazing of livestock due to the heterogeneous nature of microbial populations and nitrogen availability in soils (Conen et al., 2000; Jarecki et al., 2008; Oenema et al., 1997).

The two main flux measurement methods applied on the field scale for $\text{N}_2\text{O}$ in agricultural areas are the flux chamber
method and the eddy covariance method (e.g. Jones et al., 2011; Skiba et al., 2013). Chamber fluxes are measured over a number of enclosed areas (typically < 1 m²) on a field, and a mean or median flux estimate is extrapolated to the farm, field or regional scale: the combination of upscaling with the large spatial variability of N₂O sources often results in very significant uncertainty when estimating N₂O fluxes (Velthof et al., 1996). The advantage of using the eddy covariance method is that it can measure and integrate flux data directly over areas greater than 100 m² continuously without disturbing the soil or air environment. For large homogeneous areas, which are well represented by an integrated value of flux, the eddy covariance approach is ideal, but it does not address the issue of spatial variability on reported fluxes within the measurement area. Eddy covariance also requires fast, sensitive equipment that often demands high power supply, and so it can be an expensive option (Hensen et al., 2013).

In this experiment, a high precision dynamic chamber method (Cowan et al., 2014) was used to make 100 flux measurements of N₂O from an intensively managed grassland field which contained several features associated with elevated N₂O fluxes. Soil NH₄⁺, NO₃⁻, total carbon, total nitrogen, water filled pore space (WFPS%), bulk density and pH were recorded from 55 out of 100 flux measurement locations. The aims of the experiment were (i) to measure the spatial variability of N₂O fluxes at a field scale, (ii) to try to identify the main drivers of this variability and (iii) to provide better understanding of how N₂O flux estimates from agricultural soils can be improved.

2 Materials and methods

2.1 Field site

Flux measurements were carried out at an intensively managed grassland field owned by the University of Edinburgh (55°52′1.2144″ N, 3°12′39.564″ W) (Fig. 1). This 6.78 ha field contained approximately 140 sheep (a mixture of ewes and lambs) during the 3-day measurement period between 8 and 10 July 2013. Measurements were made continuously between 10:00 and 16:00 GMT on these days. This field had been used to graze predominantly sheep for at least the last decade with regular nitrogen fertiliser application. The field contained several interesting features that provided the opportunity to measure N₂O fluxes from soils with a wide range of properties. The vast majority of the field (98.62 % of the study area) could be classed as typical grazed grassland in which sheep were free to roam during the measurement period. The sheep had been present on the field for several months, giving us the opportunity to measure from suspected hotspots of N₂O flux where sheep droppings had collected on the grass. A drinking trough was situated in a shaded area under several large mature trees with wide leaf coverage at the north end of the field. The sheep had spent a lot of time in

**Figure 1.** The locations of 100 flux measurements (markers) made over a 6.78 ha grazed grassland field using the closed loop dynamic chamber method (bottom). Details of the high density measurement areas in the north of the field are expanded (top). Features present in the field are outlined, including the tree shaded area (Sh), the two small patches of silage remains (S1 & S2) and the manure heap (M). The stream runs across the north of the field through the shaded area.

this shaded area due to the warm weather during the past 2–3 weeks before measurements were made. This behaviour was observed during recent measurements carried out in adjacent fields unrelated to this study. Several flux measurements were made in the shaded area to investigate the effect that the recent increase in sheep density in this area had on N₂O flux.

Patches of decayed grass silage were visible in two small areas of the field. These patches remained after silage bales had been placed in the fields to feed the sheep over the winter months. The patches had scared the grassland leaving small areas of bare soil, with decayed grass matter still present. Fluxes from both of these patches were measured during the experiment. A small running stream crosses the north side of the field which helped with drainage. Several flux measurements were made from the stream using the dynamic chamber to investigate if it was a significant source of N₂O.

One particular area of interest was a large manure heap which was situated in the north-east corner of the field. This heap was a semi-permanent feature which had been used to fertilise a nearby barley field on several occasions. The heap reached a height of up to 3 m and covered approximately 100 m² of the field, with a wider perimeter of contaminated soil. The area of influence of the manure heap contamination was uncertain due to consistent build up and removal of the heap over several years. A scarred area around the heap was visible with no grass present for several metres. The scarred
grassland was used as an indicator of the area of contamination of the manure heap. Measurements were made on the heap, from soils near the base of the heap and on the contaminated soils surrounding the heap at varying distances to investigate the spatial variability of this particular feature of the field.

### 2.2 Dynamic chamber method

\(\text{N}_2\text{O} \) flux measurements were made using a non-steady-state flow-through (or closed dynamic) chamber system which circulated air between a flux chamber and a quantum cascade laser (QCL) gas analyser via an air pump (SH-110, Varian Inc, CA, USA) (for a full description of the system see Cowan et al., 2014). A compact continuous wave QCL (CW-QC-TILDAS-76-CS, Aerodyne Research Inc., Billerica, MA, USA) was used to measure gas mixing ratios within the volume of the chamber in m³. The instrument was secured inside a four wheel drive vehicle to allow mobile measurements. A diesel generator was kept on a tow trailer which provided electricity to the system. The chamber was placed onto circular aluminium collars which were inserted several centimetres into the soil (on average 5 cm) and almost flush to the soil, prior to each measurement. Neoprene sponge formed an airtight seal between the chamber and the collar. When used to measure from the stream in the field, the chamber was held steady in place by hand with the bottom slightly under the surface of the water. Two 30 m lengths of 3/8 in. ID Tygon® tubing were attached to both the inlet of the analyser and the outlet of the pump. This provided a 30 m radius from the vehicle in which the chamber could be placed. A flow rate of approximately 6 to 7 L min⁻¹ was used between the analyser and the chamber.

Fluxes of \(\text{N}_2\text{O} \) were calculated using linear and non-linear asymptotic regression methods using the HMR package for the statistical software R (Levy et al., 2011; Pedersen et al., 2010). Using a mixture of goodness-of-fit statistics and visual inspection, the regression method that provided the best fit for the time series of concentration was chosen for each individual measurement. The rate of change in the concentration of a particular gas was then used to calculate the soil flux for each measurement according to Eq. (1).

\[
F = \frac{\text{d}C}{\text{d}t_0} \cdot \frac{\rho V}{A},
\]

where \(F\) is gas flux from the soil (μmol m⁻² s⁻¹), \(\text{d}C/\text{d}t_0\) is the initial rate of change in concentration with time in μmol m⁻³ s⁻¹, \(\rho\) is the density of air in mol m⁻³, \(V\) is the volume of the chamber in m³ and \(A\) is the ground area enclosed by the chamber in m².

### 2.3 Soil sampling and analysis

Fifty-five of the 100 locations from which dynamic chamber measurements were made were selected for soil analyses. From these locations, 5 cm deep soil samples were taken from inside the chamber collar using a 2 cm wide corer immediately after the flux measurement was completed. These soils were used to calculate soil pH and available nitrogen in the form of ammonium (\(\text{NH}_4^+\)) and nitrate (\(\text{NO}_3^-\)) via KCl extraction (see below). Soil cores were taken immediately after the flux measurement using a sharp metal cutting cylinder (7.4 cm diameter, 5 cm deep) which was carefully hammered into undisturbed soil. Samples were used to calculate total carbon and nitrogen content of the soil, soil moisture content (via oven drying at 100°C) and WFPS% as well as bulk density. WFPS% was calculated from the bulk density soil samples using Eq. (2) (Rowell, 1994).

\[
\text{WFPS\%} = \frac{V_{\text{cont}} \times 100}{1 - \left(\frac{r_b}{r_d}\right)},
\]

where WFPS% is the percentage of porous volume in the soil filled by water, \(V_{\text{cont}}\) is the volumetric water content of the soil, \(r_b\) is the bulk density of the soil in g cm⁻³ and \(r_d\) is the particle density of the soil (assumed as 2.65 g cm⁻³) (Rowell, 1994).

KCl extractions were carried out on 15 g un-dried soil samples (kept frozen until extraction) using 1 mol L⁻¹ KCl solution. Concentrations of \(\text{NH}_4^+\) and \(\text{NO}_3^-\) were measured using a Bran+Luebbe AutoAnalyzer (SPX Flow Technology, Norderstedt, Germany). The mass of available nitrogen in the soil was calculated using Eq. (3).

\[
N = \frac{C \times V}{m},
\]

where \(N\) is the mass of nitrogen in the form of \(\text{NH}_4^+\) or \(\text{NO}_3^-\) in grams (per kilogram of soil), \(C\) is the concentration of \(\text{NH}_4^+\) or \(\text{NO}_3^-\) measured in the analysis of KCl extract in mg L⁻¹, \(V\) is the volume of solution in which the soil sample was mixed with KCl in L and \(m\) is the mass of dry soil mixed with the KCl solution in grams.

### 3 Results

#### 3.1 Variation in \(\text{N}_2\text{O} \) fluxes at the field scale

The 3-day measurement period (8 to 10 July 2013) was very dry with no rainfall and relatively low soil moisture contents (ranging from 9 to 50% WFPS). Daily temperatures were similar, with mean daytime soils temperatures recorded as 15.7, 16.6 and 15.9°C on the 8, 9 and 10 of July, respectively. Flux measurement locations were chosen using a mixture of a grid approximately 30 x 30 m across the field and a selection of feature areas in which multiple measurements were made in close proximity (See Fig. 1). Fifty measurements were made on what was considered “normal” grassland across the field. This provided an estimate of the spatial variability of \(\text{N}_2\text{O} \) flux across the field without interference.
from the hotspot features. Chamber placement on the grassland area included some locations where sheep droppings were present. These locations were noted during measurements when visible. Fluxes from the grassland followed a geometric (log-normal) distribution ranging between 2 and 227 µg N$_2$O-N m$^{-2}$ h$^{-1}$, with an arithmetic and geometric mean value of 25 and 13 µg N$_2$O-N m$^{-2}$ h$^{-1}$, respectively (Fig. 2). No negative fluxes of N$_2$O were measured during this experiment at any of the locations. Droppings were present at locations where the two largest fluxes were measured from the grassland (227 and 132 µg N$_2$O-N m$^{-2}$ h$^{-1}$), although fluxes measured at other locations which contained droppings were not always larger than those observed on clear (dropping-free) grassland (Fig. 2).

3.2 Silage and shaded patch fluxes

Two features which were measured in more detail were patches of the field which contained the remains of decayed grass silage and a large area shaded by trees in which the sheep had spent much of their time due to the warm weather. A total of seven flux measurements were made over two patches of decayed grass silage (Fig. 3a). Only small residues of the grass silage were visible, mixed in with the soil in these areas as the sheep had consumed the majority of it months before the measurement period. The patches were easily visible due to the lack of grass on the bare soil where the silage bales had been left. N$_2$O fluxes measured from these plots were higher than those measured from the grassland area. Fluxes varied from 1160 to 13 393 µg N$_2$O-N m$^{-2}$ h$^{-1}$ (Fig. 3a). The arithmetic and geometric mean values of these fluxes were 3745 and 2664 µg N$_2$O-N m$^{-2}$ h$^{-1}$, respectively.

Five flux measurements were made in the shaded area in which the sheep had access to a water trough. These fluxes varied between 200 and 9600 µg N$_2$O-N m$^{-2}$ h$^{-1}$ (Fig. b). The arithmetic and geometric mean values of these fluxes were 2983 and 1217 µg N$_2$O-N m$^{-2}$ h$^{-1}$, respectively. The precise area which had been influenced by increased sheep activity was difficult to measure with certainty, although an increased number of animal droppings, clumps of wool and damp urine patches were visible in this area of the field. The two measurements made in the centre of the shaded area appeared to contain more animal droppings and emit higher fluxes, whereas the outer perimeter appeared more similar to the surrounding grassland area and fluxes were lower. It was likely that the additional presence of sheep had influenced N$_2$O production in this area, although the effect of the shade (on soil moisture content) and a difference in organic material composition (due to leaf litter) provided by the tree may have also contributed.

3.3 Drainage stream fluxes

Flux measurements were made using the chamber from a stream: nine sampling points were chosen where the stream was wide enough to fit the chamber onto the surface of the water with flux values shown in Fig. 4. The stream was approximately 5 m away from the north edge of the study area. These measurements of flux were not as reliable as the measurements made on the soil, due to the unavoidable disturbance on water pressure and flow caused by the chamber. These flux estimates can still be used as a rough approximation of the N$_2$O which is emitted from the stream as it passes through this field. Fluxes from the stream varied from 1 to 22 µg N$_2$O-N m$^{-2}$ h$^{-1}$ with arithmetic and geometric mean values of 9.5 and 7.1 µg N$_2$O-N m$^{-2}$ h$^{-1}$, respectively. These fluxes were similar in magnitude to some of those measured from the grassland area, although hotspots were not observed in the stream, even in areas with higher turbulence in which de-gassing of N$_2$O would be expected to increase (Reay et al., 2003). It is not possible to determine the magnitude of N$_2$O fluxes which may have occurred further downstream as a result of inputs from the field. The measurements were
made only as an indicator of the fluxes from the stream within the field area.

3.4 Manure heap fluxes

Ten N₂O flux measurements were made directly on top of the manure heap located on the field at differing heights (0.5 to 3 m). Care was made not to physically disturb the chamber during measurements to prevent additional gases escaping from the porous manure surface. Fluxes varied in magnitude significantly across the heap with measured values ranging between approximately 660 and 79 000 µg N₂O-N m⁻² h⁻¹ (Fig. 5). Two of the measurements recorded very high N₂O fluxes exceeding 35 000 µg N₂O-N m⁻² h⁻¹. No relationship between the height of the heap and N₂O flux was observed from these measurements. Seven sampling points were taken near the foot of the heap: fluxes recorded from these locations showed a similar mixture of very large and comparatively small fluxes of N₂O, varying by up to 3 orders of magnitude, between 85 and 31 250 µg N₂O-N m⁻² h⁻¹. Again, no clear spatial pattern was observed in the fluxes around the heap. A further six flux measurements were made at distances of 5 to 10 m and five more were made at 10 to 20 m from the heap. The arithmetic and geometric mean fluxes recorded from the 5 to 10 m range were 6759 and 1986 µg N₂O-N m⁻² h⁻¹, respectively. The arithmetic and geometric mean fluxes recorded from the 10 to 20 m were 466 and 91 µg N₂O-N m⁻² h⁻¹, respectively. These results suggest that the influence of the manure heap on N₂O fluxes decreases dramatically after a distance of approximately 10 m (See Fig. 5).

3.5 Variation in soil properties at the field scale

Soil measurements were made from 55 of the 100 flux measurement locations (Table 1). The majority of these samples (n = 38) were taken from the grassland area to assess the natural heterogeneity of the soil throughout the field. The remaining soil samples were taken from the visible hotspot features of the field to investigate the causes of elevated N₂O emissions (n = 17).

The most variable of the soil properties across the grassland area were the concentrations of the available reactive nitrogen in the form of NH₄⁺ and NO₃⁻ (see Table 1). Locations with elevated NH₄⁺ also generally recorded higher NO₃⁻ concentrations, although this relationship was not consistent at all locations (R² = 0.56). Soil samples taken from patches of decayed grass silage and the shaded area indicated that these small areas had significantly greater concentrations of NH₄⁺ and NO₃⁻ (p < 0.001) compared to the grassland area. Reactive nitrogen concentrations in soils from the perimeter of the manure heap also showed wide variations, with some extremely large (2.2 g N kg⁻¹) and small (0.1 g N kg⁻¹) values being measured (Table 1).

Total carbon and nitrogen content of the soil from the grassland area showed less variation than the reactive nitrogen content, with a small number of elevated outlier values. The ratio of carbon to nitrogen content of the soils (12 : 1) was consistent across the measurement locations (R² = 0.94). Total soil carbon and nitrogen concentrations from the shaded area and silage remains were similar in magnitude to the grassland area measurements. The manure heap perimeter was the exception to this, presenting some very...
high concentrations of carbon and nitrogen. Total carbon and nitrogen content of the soils around the manure heap varied from small concentrations similar to the grassland soil (8 and 107 g C kg\(^{-1}\)) to concentrations as large as 34 and 355 g C kg\(^{-1}\) (Table 1). Soil pH varied little between most of the measurement locations in the grassland area with the majority of the grazed field confidently estimated at pH levels of 5.6 ± 0.34 (n = 38), in agreement with measurements made in similar managed grazed fields in this area. Soil pH from the silage remains and tree shaded area was generally more alkaline (pH 6.9 ± 1.5) than from the grassland area. The soils from the manure heap perimeter were highly alkaline (pH 8.3 ± 0.85) (Table 1).

WFPS\% values across all measurement locations in the field ranged between 9 and 50 % with a mean value of 26.5 %. The bulk density of the soil in the field with the exception of the manure heap perimeter ranged between 0.6 and 1.1 g cm\(^{-3}\) with a mean value of 0.8 g cm\(^{-3}\). Due to the heterogeneous nature of soils there were several outliers for each of the soil properties measured across the field (Table 1).

### 3.6 Correlation between soil properties and \(\text{N}_2\text{O}\) flux

Multiple linear regression was used to investigate the relationships between the soil properties presented in Table 1 (also soil porosity) and \(\text{N}_2\text{O}\) flux. Due to the wide ranging and uneven distribution of values measured for both \(\text{N}_2\text{O}\) flux and soil properties, the common logarithm (hereafter referred to as \(\log_{10}\)) of several of these measurements (\(\text{N}_2\text{O}\) flux, \(\text{NH}_4^+\), \(\text{NO}_3^-\), total carbon and total nitrogen content) was used for the multiple linear regression. Correlations of soil properties were carried out with multiple linear regression analysis using the statistical software R. The soil properties from all of the features in the field were processed together as one group (n = 55).

Linear regression was carried out firstly using all of the measured soil properties for each of the fits. After the initial fit, the properties which were not statistically significant \((p > 0.1)\) were removed and the fit was run again using only the significant values (See Table 2). Concentrations of \(\text{NH}_4^+\) in soils were found to correlate well with pH and total carbon and nitrogen \((R^2 = 0.64; \text{Fig. 6a})\). High total carbon and nitrogen concentrations were indicative of an increased presence of total organic carbon (TOC) in the soils.

Concentrations of \(\text{NO}_3^-\) correlated strongest with TOC, \(\text{NH}_4^+\) total nitrogen and WFPS\% present in the soil \((R^2 = 0.77; \text{Fig. 6b})\). \(\text{NO}_3^-\) concentrations were presumed to be indicative of microbial nitrification activity in the soil as it is the primary product of this process. Fluxes of \(\text{N}_2\text{O}\) \((\log_{10}(\text{N}_2\text{O}))\) correlated strongly with \(\text{NO}_3^-\), pH and WFPS\% \((R^2 = 0.86; \text{Fig. 6c})\). The soil property with the most significant correlation with \(\text{N}_2\text{O}\) flux was \(\text{NO}_3^-\) (See Table 2).

### 3.7 Interpolation of \(\text{N}_2\text{O}\) fluxes at a field scale

The simplest way to estimate the total daily \(\text{N}_2\text{O}\) flux from the field during the measurement period is to combine the relevant area and mean flux recorded for each of the features of the field. Due to the uneven distribution of flux magnitude and the many large hotspots of flux measured using the chamber method in this experiment, geometric mean values are most suitable to determine values across the field scale (Table 3). Using the geometric mean values, an estimate of 47.7 g \(\text{N}_2\text{O}\)-
Flux magnitude was unpredictable across the grassland and in some cases varied by 2 orders of magnitude across relatively short distances (< 10 m). Eighty percent of the fluxes estimated which comes from a relatively small area of the field (excluding the hotspot areas) were highly variable (0.8 %; Table 3).

### 4 Discussion

#### 4.1 Variation in N₂O fluxes at the field scale

N₂O fluxes measured from the grazed grassland area of the field (excluding the hotspot areas) were highly variable (between 2 and 227 µg N₂O-N m⁻² h⁻¹). This is a common phenomenon which is verified in many N₂O flux measurement experiments (e.g. Oenema et al., 1997; Skiba et al., 2013). Flux magnitude was unpredictable across the grassland and in some cases varied by 2 orders of magnitude across relatively short distances (< 10 m). Eighty percent of the fluxes measured from the grassland area were below 30 µg N₂O-N m⁻² h⁻¹. Fluxes of N₂O comparable to this magnitude are often measured from grazed fields in different climates in between fertilisation events (Clayton et al., 1997; Luo et al., 2013; Oenema et al., 1997). The advantage of using the closed loop dynamic chamber (Cowan et al., 2014) in this experiment was that the extremely high precision (1 µg N₂O-N m⁻² h⁻¹) allowed us to confidently report very low individual N₂O fluxes across the field and compare these measurements with the relevant soil properties collected from within the measurement plot at each individual location.

The largest fluxes in the field were measured from the hotspot features present (up to 79 000 µg N₂O-N m⁻² h⁻¹). Fluxes from the shaded area and the silage heap remains were consistently higher than those measured on the grassland area. The shaded area presented an increased number of sheep, with the resultant increase in animal waste freshly deposited there (NH₄⁺). Fluxes measured from the silage heap remains were surprisingly high. Decaying plant matter is known to emit N₂O (Hellebrand, 1998), but it is unclear whether the emissions from these patches are due to the additional organic materials present in the soil or to the increased sheep activity and resultant urine and faeces deposits. The larger pH values from the shaded areas, as well as the manure heap and perimeter suggest that animal waste deposited there (NH₄⁺) contributed a very large 38 % (18 g N₂O-N) of the total flux estimate which comes from a relatively small area of the field (0.8 %; Table 3).

### Table 2. Multiple linear regression correlation of soil properties and N₂O flux as plotted in Fig. 6.

<table>
<thead>
<tr>
<th></th>
<th>Estimate</th>
<th>SD</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ( Y = \log_{10}(\text{NH}_4^+) )</td>
<td>Intercept</td>
<td>-2.56</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>0.37</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{Carbon g Kg}^{-1}) )</td>
<td>-1.14</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{Nitrogen g Kg}^{-1}) )</td>
<td>1.53</td>
<td>0.79</td>
</tr>
<tr>
<td>(b) ( Y = \log_{10}(\text{NO}_3^-) )</td>
<td>Intercept</td>
<td>-402.47</td>
<td>205.04</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{NH}_4^- - \text{N g Kg}^{-1}) )</td>
<td>0.48</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{Carbon g Kg}^{-1}) )</td>
<td>-6.7</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{Nitrogen g Kg}^{-1}) )</td>
<td>8.58</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>WFPS%</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Soil porosity</td>
<td>403.81</td>
<td>205.12</td>
</tr>
<tr>
<td></td>
<td>Bulk density g cm⁻¹</td>
<td>154.86</td>
<td>77.39</td>
</tr>
<tr>
<td>(c) ( Y = \log_{10}(\text{N}_2\text{O Flux}) )</td>
<td>Intercept</td>
<td>-4.33</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{NH}_4^- - \text{N g Kg}^{-1}) )</td>
<td>-0.25</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>( \log_{10}(\text{NO}_3^- - \text{N g Kg}^{-1}) )</td>
<td>0.76</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>0.60</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>WFPS%</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Soil porosity</td>
<td>3.85</td>
<td>1.34</td>
</tr>
</tbody>
</table>

The manure heap and soils contaminated by the heap contributed a very large 38 % (18 g N₂O-N) of the estimated daily N₂O flux from the field. The silage remains and shaded area contributed 5 and 13 % to the total emissions, respectively. The manure heap and soils contaminated by the heap contributed a very large 38 % (18 g N₂O-N) of the total flux estimate which comes from a relatively small area of the field (0.8 %; Table 3).
Bouwmans, 2005; Saggar et al., 2013), which is most probably the main source of the N$_2$O here.

Fluxes of N$_2$O from the stream were relatively small (1 to 22 µg N$_2$O-N m$^{-2}$ h$^{-1}$) compared with those measured from the rest of the field. Significantly higher fluxes have been measured from drainage streams at the Bush Estate in previous experiments (100 to 1000 µg N$_2$O-N m$^{-2}$ h$^{-1}$) using a different methodology (Reay et al., 2003). Dry conditions in the run up to the measurement period had decreased any leachate from the soils entering the stream. Past experiments have reported N$_2$O flux measurements from agricultural streams similar in magnitude to those made in the surrounding soils (Baulch et al., 2011); however, it is likely that the N$_2$O fluxes measured in this experiment are lower than they would have had the measurements taken place on a wetter date when drainage waters containing N$_2$O and other nitrogen compounds from surrounding fields would also have been entering the stream.

Flux measurements made on and around the manure heap were on average 420 times higher than the fluxes measured for the grassland area of the field. The large spatial variability of N$_2$O flux observed from the heap was similar to that of a previous experiment carried out on the farm estate using static chamber measurements, although reported fluxes are an order of magnitude smaller in this study (Skiba et al., 2006). Solid manure heaps are a known large source of N$_2$O emissions and several studies have estimated emission factors for such heaps (Amon et al., 2001; Chadwick et al., 1999; Skiba et al., 2006). Emission factors for manure heaps are often calculated by volume of stored manure. This implies a large degree of variability, following from the different components of animal waste as well as the age of the waste and how it is stored (Amon et al., 2001). Application of the manure as fertiliser is often considered in the emission factor of animal waste as well as storage (Chadwick et al., 1999, 2011; Velthof et al., 2003). Measurements made in this experiment did not account for manure volume or calculate an emission factor for the heap; however, this study highlights that an additional factor may also need to be taken into account for a more accurate estimate of the emission factor of solid manure storage (i.e. the legacy emissions of a manure heap). Very high N$_2$O fluxes (up to 10 825 µg N$_2$O-N m$^{-2}$ h$^{-1}$) were measured from the area around the manure heap which had become contaminated with the animal waste. Our data have shown that these areas that are highly enriched with available nitrogen compounds, and organic matter remain after the manure heap has been removed and can continue to emit N$_2$O for months, as was observed for the patches of silage heap remains (manure was spread in autumn, 9 months prior to measurements). The high emissions and lasting effect of these areas may contribute significantly to the overall emission factor of solid manure heaps and agriculture as a whole when the large volumes of animal waste and storage from livestock farms are considered.

### 4.2 Correlation between soil properties and N$_2$O flux

High concentrations of NH$_4^+$ and NO$_3^-$ are known to increase N$_2$O fluxes from soils as they are the primary nutrients required for the microbial processes of nitrification and denitrification in which N$_2$O is produced and then released into the atmosphere (Davidson et al., 2000). Animal urine and droppings are a known source of urea CO(NH$_2$)$_2$ and ammonia (NH$_3$), which are both alkaline and convert to NH$_4^+$ in the presence of water (Freney et al., 1983). A strong positive correlation between NH$_4^+$ concentrations and soil pH was observed across the field (See Table 2). As ruminant (sheep and cattle) urine is normally slightly alkaline, the increased pH in the small hotspot areas suggested that increased alkaline animal waste deposition was the reason for the increase in pH and resultant available NH$_4^+$ in the soil. This relationship has also been observed in other studies (e.g. Haynes and Williams, 1992). Organic matter in the soils (total C and N) also correlated with NH$_4^+$ concentrations in the soils (See Table 2). Mineralisation of animal waste, and plant materials such as silage, continues to provide NH$_4^+$ to soils over extended periods (Martins and Dewes, 1992; Van Kessel and Reeves, 2002). All of the N$_2$O flux hotspot features of the field contained elevated concentrations of NH$_4^+$ in the soil.
There remains a high degree of uncertainty in the relationship between the soil properties and $\text{N}_2\text{O}$ flux. This study suggests $\text{NH}_4^+$, $\text{NO}_3^-$ and organic matter can be used as proxies to predict where fluxes will be higher in the field; however, exact fluxes are more difficult to estimate due to the large number of variables which affect the rates of microbial processes. Many studies have identified similar soil properties which affect the rate of $\text{N}_2\text{O}$ emissions from agricultural soils (Butterbach-Bahl et al., 2013; Dobbie and Smith, 2003); however, due to the multiple simultaneous microbial processes which produce $\text{N}_2\text{O}$ it is difficult to identify a clear relationship between soil properties and flux. Relationships between $\text{N}_2\text{O}$ flux with temperature, WFPS% and nitrogen content in soils are often observed, yet a consistent method for predicting $\text{N}_2\text{O}$ from agricultural soils based on soil measurements still eludes researchers (Flechard et al., 2007; Smith et al., 2003).

Multiple linear regression correlation between flux and soil properties reported in studies similar to our own predicted very different significance values for each of the measured soil properties depending on environmental factors (Šimek et al., 2006; Turner et al., 2008). In order to advance our understanding of these processes, more detailed experiments are required in a variety of geographical and environmental conditions to better predict the behaviour of microbial processes in soils with high available nitrogen concentrations. Alternatively, a more controlled analysis of individual soil properties and microbial processes can be examined under laboratory conditions using similar high precision chamber methodology. Ideally the use of this equipment could be paired with $^{15}$N labelled nitrogen compounds (such as urea) and denitrification inhibitors to investigate the biological mechanisms in $\text{N}_2\text{O}$ production and determine relationships between these processes and soil properties.

### 4.3 Interpolation of $\text{N}_2\text{O}$ fluxes at a field scale

Using mean values to interpolate $\text{N}_2\text{O}$ flux at the field scale results in very high uncertainty values due to the high spatial variability of the $\text{N}_2\text{O}$ fluxes (Table 3). From this experiment, the total daily flux is estimated to be between 12.8 and 215.1 g $\text{N}_2\text{O}$-N d$^{-1}$. These high uncertainties highlight the weakness of the chamber methodologies inability to account for spatial variability of $\text{N}_2\text{O}$ flux over large areas and the importance of spatial variability when $\text{N}_2\text{O}$ flux estimates are made using simple interpolation methods on a large scale. These results also highlight the need for a better understanding of how agricultural flux measurements are made using current methodology. Flux chamber placement is vital in understanding the variability of $\text{N}_2\text{O}$ flux across a field. Without a good understanding of $\text{N}_2\text{O}$ hotspots and the appropriate positioning of chambers to include (or exclude) these areas, chamber methods will not be able to provide effective comparable results between experiments.
The nature of the unpredictable spatial variability in the flux or the corresponding soil properties across the field is the distance between measurement locations in metres and the y axis is the semivariance in all of the respective measurements made for the entire field. Variance diagrams highlight this lack of predictability across the field, showing a random distribution with no clear spatial pattern visible are much more difficult to investigate. Variance diagrams highlight this lack of predictability across the field, showing a random distribution with no clear spatial pattern visible in the flux or the corresponding soil properties across the field (Fig. 7). The nature of the unpredictable spatial variability of N2O fluxes is a huge barrier which limits the use of many methods of spatial interpolation of the flux across a large scale such as a field. Taking many chamber measurements across a small area is one way to improve this method (Turner et al., 2008); however, this becomes impractical at larger scales and a compromise needs to be made between field coverage and the number of chamber measurements taken.

Another method of measuring N2O fluxes at a field scale which has advanced in recent years due to the increasing precision of rapid gas analysers would be eddy covariance (Eu-gster et al., 2007; Kort et al., 2011). Eddy covariance does not suffer from the same interpolation issues as the chamber method and can provide a relatively confident estimate of mean N2O flux across a large area (> 100 m²). The weakness of the eddy covariance method is that it would not be able to distinguish between sources and provide information on hotspot fluxes. Areas in which animals spend a lot of time to shelter from the elements such as the shaded area in this field-scale study present problems for eddy covariance measurements as any physical objects which alter turbulence in the air (such as trees or foliage in our case) can prevent measurements from taking place. From the results in this experiment we would suggest that both methods should be deployed in tandem to investigate N2O flux at the field scale as both methods have significant weaknesses that the other can compliment.

5 Conclusions

Spatial variability remains one of the largest sources of uncertainty when measuring N2O flux from agricultural soils. Results from this study suggest that additional nitrogen applied to fields in the form of animal waste is the primary source of anthropogenic N2O emissions from grazed agricultural soils (with the exception of fertiliser events). The wide and often random distribution of this nitrogen in the soils is one of the major causes of the spatial variability observed in N2O emissions. This inherent variability of soil properties limits the ability to reduce uncertainty in N2O emission estimates that can be achieved by taking a practical number of flux measurements using a chamber method. In order to reduce uncertainties in large-scale emission budgets, it is effective to identify hotspots of N2O fluxes and determine the causes of these increased emissions. Identifying areas in which N2O fluxes are significantly higher than the majority of the experimental area can reduce overall uncertainty in results by defining different emission factors.

This study highlights the requirement of a better understanding of spatial variability of N2O fluxes from intensively grazed grasslands. Without a basic understanding of how hotspots of N2O are formed and the lifetime of these emissions from agricultural contributions to N2O emissions are often dominated by emission factors which account for the soil conditions of the majority of the area of a field. These budgets may be significantly underestimating N2O fluxes in some cases, especially for livestock farms with high stocking densities.

Author contributions. N. Cowan, P. Norman and U. Skiba designed the measurement strategy for the experiment. The field measurements and soil analysis were carried out by N. Cowan and P. Norman. N. Cowan carried out the statistical analysis of the data with help from D. Famulari and P. Levy. D. Famulari and P. Levy also provided help with instrumentation and methodology. N. Cowan and U. Skiba prepared the manuscript with contributions from all of the co-authors. The study was carried out under the supervision of U. Skiba and D. Reay.
Acknowledgements. We thank the University of Edinburgh farm, especially Wim Bosma for providing the field site and farm data. We also thank DEFRA and the UK Devolved Administrations for financial support through the UK GHG Platform project AC0116 (The InveN2Ory project).

Edited by: E. Veldkamp

References