Nitrogen use efficiency and N_2O and NH_3 losses attributed to three fertiliser types applied to an intensively managed silage crop

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Abstract

Three different nitrogen (N) fertilizer types, ammonium nitrate, urea and urea coated with a urease inhibitor (Agrotain®), were applied at standard rates (70 kg N ha^{-1}) to experimental plots in a typical and intensively managed grassland area at Easter Bush Farm Estate (Scotland). The nitrogen use efficiency of the fertilisers was investigated as well as nitrogen losses in the form of nitrous oxide fluxes (N_2O) and ammonia (NH_3) during fertilisation events in the 2016 and 2017 growing seasons. Nitrous oxide was measured by the standard static chamber technique and analysed using Bayesian statistics. Ammonia was measured using passive samplers combined with the FIDES inverse dispersion model. On average, fertilisation with ammonium nitrate supported largest yields and had the highest nitrogen use efficiency, but as large spatial and seasonal variation persisted across the plots, yield differences between the three fertilizer types and zero N control were not consistent. Overall, ammonium nitrate treatment was found to increase yields significantly (p-value < 0.05) when compared to the urea fertilisers used in this study. Ammonium nitrate was the largest emitter of N_2O (0.76 % of applied N) and the urea was the largest emitter of NH_3 (16.5 % of applied N). Urea coated with a urease inhibitor did not significantly increase yields when compared to uncoated urea; however, ammonia emissions were only 10 % of the magnitude measured for the uncoated urea, and N_2O emissions were only 47 % of the magnitude of those measured for ammonium nitrate fertiliser. This study suggests that urea coated with a urease inhibitor is environmentally the best choice in regards to nitrogen pollution, but because of its larger cost and lack of agronomic benefits, it is not economically attractive when compared to ammonium nitrate.

1. Introduction

Due to a large and rapidly expanding global population, modern-day agriculture requires regular inputs of industrially produced reactive nitrogen fertilisers (Nr) (i.e. nitrogen compounds that plant life can consume through root systems such as ammonium nitrate (AN) and urea) in order to keep up with increasing food demand (Lassaletta et al., 2014). This wide-scale intensive application of Nr has resulted in significant anthropogenic alterations of virtually every process in the natural global nitrogen cycle (Fowler et al. 2013; Vitousek et al., 1997). Typically, more than half of applied Nr is lost to the environment through various biological pathways and chemical processes (Lassaletta et al., 2014; Raun and Johnson 1999), such as nitrate (NO_3^-) run-off into streams and waterways (Lu and Tian 2017) as well as gaseous losses in the form of ammonia (NH_3) (Bouwman et al., 1997), nitrous oxide (N_2O) (Reay et al., 2012), and nitrogen oxides (NO_x) (Bertram et al. 2005). This relatively low nitrogen use efficiency (NUE) results in significant environmental damage at a global scale.

After fertiliser application, the resulting volatilization of NH_3, especially from urea, will often contaminate the surrounding environment with deposition of Nr, in some cases causing significant damage to fragile biodiversities by increasing nitrogen loading (Phoenix et al. 2006). Fluxes of NH_3 also contribute to an increase of particulate matter ($PM_{2.5}$) in the atmosphere which has negative implications for human health (Paulot and Jacob 2014). Agricultural sources contribute an estimated 60 % of global anthropogenic N_2O emissions (Syakila and Kroeze 2011), primarily due to increasing the quantity of Nr in soils and aquatic systems in which N_2O is released as a byproduct of the microbial processes of nitrification and denitrification (Davidson et al. 2000). N_2O is a potent greenhouse gas as well as the most significant contributor to global stratospheric ozone depletion (Ravishankara et al., 2009) which doubly increases the incentive to mitigate these emissions.

Current projections predict that global rates of Nr fertiliser will continue to rise over the next century in order to cope with a growing population and an increase in meat production (FAO, 2017), and therefore, it has become increasingly urgent to address the issue of nitrogen pollution from agriculture sources. However, food supply is a sensitive issue both politically and economically, with limited options available to governments or environmental regulators that may attempt to mitigate the damage caused by agricultural nitrogen pollution. One favorable option which potentially benefits all parties is to attempt to increase the NUE of Nr applied to crops, therefore maintaining high yields while reducing Nr lost to the environment in its various damaging forms. Typically, when fertiliser is applied, the water soluble nitrogen compounds permeate into the rhizosphere allowing plant roots to absorb the nitrogen and the microbial community to convert Nr through the processes of nitrification and denitrification into gaseous compounds (N_2O, NO_x & N_2) which may then be lost to the atmosphere (Davidson et al., 2000). In theory, by slowing the release of the Nr, plants can outcompete the microbial populations and less N escapes into air and ground waters as leachate. This can result in increased NUE, decreased environmental impact, improved crop yields and reduced fertiliser costs for farmers making these efforts an attractive prospect for combatting global nitrogen pollution.

Several methods have been tested to slow down the release of Nr from synthetic fertilisers. In its simplest form, this can be achieved by increasing the particle size of the applied fertilizer pellets (Azeem et al., 2014; Shamsudin et al., 2014). More complicated methods of Nr inhibition come in the form of microbial inhibitors which directly target and slow a specific biological pathway (Abalos et al., 2014; Modolo et al., 2015). Synthetic fertilisers (typically urea) coated with chemical inhibitors that target urease hydrolysis and microbial nitrification are already commercially available.

Microbial inhibitors have been shown to reduce Nr losses for both N_2O and NH_3 under laboratory conditions and in field trails, but with varying success (Sanz-Cobena et al., 2016; Ni et al., 2014; Singh et al., 2013; Rose et al., 2017; Ruser and Schulz 2015). Although there are positive studies which promote the pollution reducing capabilities of these chemicals (Misselbrook et al., 2014), some questions remain over the overall effectiveness of the inhibitors which face claims that reduction of one form of Nr pollution may increase another. This is most commonly observed for nitrification inhibitors in which the slowing on the conversion of NH_4^+ to NO_3^- in soils results in a decrease in N_2O at the expense of an increase in NH_3 volatilisation (Lam et al., 2016; Zaman et al., 2009). In theory, the use of a urease inhibitor should reduce both the emission of NH_3 by reducing the rate at which urea is converted to NH_4^+ in soils, thus limiting available nitrogen in all forms. This may however, limit the rate at which crops also receive Nr and reduce yields. The use of inhibitors in farming remains uncommon, mostly due to a reluctance to change to an uncertain practice, compounded by the drawback that treated fertilisers are typically more expensive than traditionally used products. Further work using specific products in different environments is needed to supply evidence that will provide the agricultural community with the confidence to make the changes required to meet future NUE demands globally.

This study aims to specifically investigate the effect of the Agrotain® urease inhibitor (Koch, KS, USA) on a typical grassland silage crop in Scotland, comparing it with the two most commonly used synthetic nitrogen fertilisers: Ammonium nitrate (Nitram®) and urea. Grasslands account for approximately 60 % of agricultural land use in the UK (approximately 74,000 km^2) to which an estimated 120 kt of ammonium nitrate and 26 kt of urea are applied annually (BSFP, 2017). The results presented in this study are intended to represent to some extent this large coverage of agricultural land in the UK to which urease inhibitors may be applied in the future.

In this study we aim to:

- Compare the nitrogen use efficiency of equivalent applications of pellet fertilisers in the form of ammonium nitrate (Nitram), urea and urea with a urease inhibitor (the percentage of applied nitrogen fertiliser that is converted into plant matter as a result of increased crop growth).
- Investigate differences in crop quality and yield as a result of the fertilisers applied.
- Quantify gaseous losses of nitrogen from the fertiliser types in the form of NH_3 and N_2O.

2. Materials and methods

2.1. Experimental Design

Fieldwork was carried out between May 2016 and September 2017. During this time, five applications of three different nitrogen fertiliser types were added to a grid of experimental plots (including a control) in intensively managed silage grassland fields (*Lolium perenne L.*) at Easter Bush Farm (Midlothian, UK, 55°51'57.4"N 3°12'29.3"W). The three fertiliser types used in the experiment were ammonium nitrate pellets (Nitram, $NH_4^+NO_3^-$), urea pellets, and urea pellets with a coating of powdered urease inhibitor (N-(n-butyl) thiophosphoric acid Triamide; Agrotain®). In 2016, fertiliser was applied twice to experimental plots known as the Engineers Field (Cowan et al., 2016). In 2017, fertiliser was applied three times to experimental plots in an adjacent similarly managed field (known as the Upper Joiner field).

The soil in both fields is classified as a clay loam for the top 30 cm in fields, with a pH (in H_2O) of 6.5 and 6.1 for the Engineers and Upper Joiner fields, respectively. They are classed as an imperfectly drained Macmerry soil of the Rowanhill association (eutric cambisol, FAO classification). All fertiliser applications were of 70 kg N ha^{-1} (Table 1) which was consistent with the typical management regime of the fields. Both fields are used as grazing pastures for mainly sheep at high stocking densities of approximately 20 ewes per hectare. The sheep were vacated before and throughout the duration of the experiment and instead the grass was grown for silage. While sheep were vacated from the 2016 field a month prior to the experiment, the 2017 plots had not been grazed for more than six months before the experiment.

For each of the five fertiliser events there were a total of sixteen plots; four treatments (including the control) replicated four times. The layout of the experimental plots varied in the two different fields. In 2016 the sixteen (Engineer's Field) plots were separated into strips of 2 m by 8 m (with a 0.5 m spacing between them). The treatments were assigned a random plot position in order to capture the spatial variability across the experimental area during measurements. In contrast, in 2017 the (Upper Joiner Field) plots were arranged in a square grid, each measuring 20 m by 20 m with no spacing between them. The treatments were also assigned at random across the grid in 2017 to capture spatial variability. For each fertiliser event the grass was allowed to grow for as long as the farm manager recommended for a full harvest (weather dependent), then all plots were harvested on the same day (see Table 1).

2.2. Crop Yield and Quality Measurements

Each of the plots was harvested and above-ground biomass was dried at 60 ^oC for 24 hours and both wet and dry weights were recorded. For the smaller 2016 plots, a 1 m^2 section of each plot was harvested manually using sheers (i.e. 1 sample per plot). For the larger 2017 plots, a small harvester

with onboard weighing capabilities (Haldrup F-55) was able to harvest an area of 30 m^2 from which yield data were obtained. After wet yield was recorded, subsamples were taken from each of the individual plots for further analysis (at SRUC Analytical Services, Midlothian, UK). The dry matter content, metabolizable energy (ME), crude protein, modified acid detergent (MAD), decimal reduction time (D value), total carbon and total nitrogen contents were all analysed from the subsamples.

The nitrogen use efficiency (NUE) reported in this study refers to the crop uptake efficiency of the total nitrogen fertiliser applied. This was calculated by subtracting the mean total nitrogen content of the harvested grass from the control plots from the mean of the treatment plots for each individual event. The NUE for each treatment was then calculated by dividing this difference by the input of N fertiliser for a known area, thus providing the overall impact of the fertiliser on crop growth. Uncertainties in in these values are represented by 95 % confidence interval of the mean, calculated by multiplying the standard deviation by 1.96. The least squares method is used to combine uncertainties when subtraction or addition is used.

2.3. N_2O Flux Measurements

Measurements of N_2O fluxes were taken for both 2016 and 2017 experiments using the static chamber approach. The chambers consisted of a cylindrical polyvinyl chloride (PVC) plastic pipe of 38 cm inner diameter (ID) and 22 cm height fitted with a sealed lid and a flange at the base. The chambers were placed onto a plastic flanged collar that had been inserted several centimeters into the soil (on average 5 cm) to form a seal in the soil. A layer of draught sealant material held in place by four strong gripping clips formed an airtight seal between the chamber and the collar for the duration of the flux measurement. Chambers were closed for 60 min, during which time four gas samples were collected via a syringe and a three-way tap fitted to the lid, at t = 0, 20, 40 and 60 minutes. Gas samples were stored in 20 ml glass vials which were flushed with 100 ml of air from the syringe using a double needle. Samples were analysed using gas chromatography (7890B GC system fitted with an electron capture detector, Agilent Technologies, UK), with a limit of detection of 7 ppb (Drewer et al., 2017). Measurements were carried out daily for two weeks after fertilisation, then every second day for a further two to four weeks. Measurements were made only on working days (Monday to Friday) between 09:00 and 15:00 GMT.

Fluxes were calculated as:

$$F = \frac{dC}{dt} . \frac{\rho V}{A} \quad \text{(Eq. 1)}$$

where F is the gas flux from the soil (nmol m^{-2} s^{-1}), dC/dt is the rate of change in the concentration in time in nmol mol^{-1} s^{-1} estimated by linear regression, ρ is the density of air in mol m^{-3}, V is the volume of the chamber in cubic meters and A is the ground area enclosed by the chamber in square meters.

Cumulative fluxes over the experimental periods (30 days) were calculated using a Bayesian approach, taking into account the log-normal distribution of spatial samples and the lognormal peak-and-decay pattern in time (Levy et al., 2017). Based on the assumption that at a given time, N_2O fluxes, F, are typically log-normally distributed in space, the probability density is given by:

$$f(F) = 1/(\sqrt{(2\pi)}\sigma_{\log}F)\exp(-((log(F) - \mu_{\log})^2/(2\sigma_{\log}^2))) \quad \text{(Eq. 2)}$$

where $\mu_{\log}$ and $\sigma_{\log}$ are the location and scale parameters, equivalent to the mean and standard deviation of the log-transformed variate.

Following a fertilisation event, the time course of N_2O flux is expected to rise to a peak, then decay exponentially, and this basic pattern is reproduced by all process-based models (i.e. Li et al., 1992; Del Grosso et al., 2006) and is also well described by the log-normal equation:

$$\mu_t = 1/(\sqrt{(2\pi)}kt)\exp(-((\log(t) - \Delta)^2/(2k^2))) \cdot N_{in}\Omega \quad \text{(Eq. 3)}$$

where μ_t is the spatial mean of the N_2O flux at time t, Δ and k are analogues for the location and scale parameters, and with the additional term N_{in} is the fertiliser nitrogen input and Ω is the fraction of this which is emitted as N_2O as t tends toward infinity. Δ can be interpreted as the natural logarithm of the delay between fertiliser application and peak flux; k is a decay rate term. So, at time t following fertilisation, the mean flux is given by:

$$\mu_{\log,t} = \log(\mu_t) - 0.5\sigma_{\log}^2 \quad \text{(Eq. 4)}$$

The parameters μ, $\mu_{\log}$ and $\sigma_{\log}$ were estimated using the Markov Chain Monte Carlo (MCMC) method with Gibbs sampling (Gelman, 2013). This was implemented using the freely available JAGS software (Plummer, 2016). The prior distribution for Ω was based on the data collated by Stehfest and Bouwman (2006). The prior distributions for Δ and k were based on the dynamics of the DNDC model (Li et al., 1992, as described in Levy et al., 2017). To obtain the cumulative flux at time t, we use the standard log-normal cumulative distribution function:

$$F_{cum,t} = \Phi\left(\frac{\ln t - \Delta}{k}\right) N_{in}\Omega \quad \text{(Eq. 5)}$$

where Φ is the cumulative distribution function of the standard normal distribution.

To account for background fluxes (fluxes of N_2O expected in the absence of any applied nitrogen), a cumulative background flux was estimated using the mean of the fluxes measured from the control plots during each event. This cumulative background estimate was then subtracted from

the cumulative fluxes estimated for each treatment. The reported EFs in this study take background fluxes into account when reporting final values.

2.4. NH_3 Flux Measurements

During the 2016 measurements we were unable to obtain wind tunnels to measure NH_3 flux as originally planned. Therefore, in 2017 fluxes of NH_3 were derived using the FIDES inverse dispersion model as described in detail in Loubet et al. (2010 & 2017). This approach requires relatively large plots (20 m^2), and according to the farmers requirements needed to be set up in the Upper Joiner field, diagonally opposite from the Engineers field. The basis of the model is the solution of the advection-diffusion equation by (Philip 1959), assuming power law profiles for the wind speed (U(z)) and the vertical diffusity ($K_z(z)$). The model assumes that the atmospheric NH_3 concentration (χ in µg NH_3 m^{-3}) at a given point (x, y, z) is the sum of the background concentration (χ_{bgd} in µg NH_3 m^{-3}) unaffected by the sources, and the influence of the sources (Equation 6). The latter is equal to all the source strengths per unit surface area (S in µg NH_3 m^{-2} s^{-1}) at locations (x_s, y_s, z_s) multiplied by the dispersion function ($D(x_s, y_s, z_s|x, y, z)$ in s m^{-1}), which expresses the contribution of each source to each receptor point at which the concentration is considered. The meaning of $D(x_s, y_s, z_s|x, y, z)$ can be viewed simply as the concentration at location (x, y, z) for a source of unit strength at location (x_s, y_s, z_s). (Loubet et al. 2010, 2017)

$$\chi_{model}(x, y, z) = \chi_{bgd} + \int_{all\ x_s\ and\ y_s} S(x_s, y_s, z_s) D(x_s, y_s, z_s|x, y, z) \quad \text{(Eq. 6)}$$

In order to calculate S, D was computed by the model, and both χ and χ_{bgd} were measured. To calculate D, the description of Philip (1959) was followed as shown in Equation 7 – 10. Here, the values of a, b, p and n are derived from a linear regression between ln(U), ln(K_z) and ln(z), over the height range 2 × z_0 to 20 m, using U(z) and $K_z(z)$ estimated based on the Monin-Obukhov similarity theory (e.g. Kaimal & Finnigan, 1994), where z_0 denotes the roughness length. In Equation 9, X = (x − x_s) sin(WD) − (y − y_s) cos(WD), and Y = (x − x_s)cos(WD) − (y − y_s) sin(WD), where WD is the wind direction; α = 2 + p − n, ν = (1 − n)/α, and $I_{-\nu}$ is the modified Bessel function of the first kind of order −ν. Finally, in Eq. 10 C_y and m are parameters taken from Sutton (1932).

$$U(z) = az^p \quad \text{(Eq. 7)}$$

$$K_z(z) = bz^n \quad \text{(Eq. 8)}$$

$$D(X, Y, z) = \frac{1}{\sigma_y\sqrt{2\pi}} exp\left(-\frac{Y^2}{2\sigma_y^2}\right) \times \frac{z z_s^{(1-n)/2}}{baX} \times exp\left(-\frac{a(z^\alpha + z_s^\alpha)}{ba^2X}\right) \times I_{-\nu}\left(\frac{2a(zz_s)^{\alpha/2}}{ba^2X}\right) \quad \text{(Eq. 9)}$$

$$\sigma_y = \frac{1}{\sqrt{2}} C_y x^{(2-m)/2} \quad \text{(Eq. 10)}$$

Wind data were recorded by two sonic anemometers (IRGASON, Campbell Scientific, UT, USA) which were positioned at the north east and south west sides of the plots, 30 m from the borders of the plots in alignment with the two wind predominant wind directions. The anemometers measured 3D wind components at 10 Hz. Following Loubet et al. (2001), the source height was tuned to $z_s = 1.01\ z_0 + d$, where d is the displacement height, in order to insure best comparison with Lagrangian Stochastic models and experiments (see also Loubet at al. 2010). The dispersion model embedded in FIDES is essentially similar to the Foken and Meixner (2001) footprint model, except for the retrieval of the a, b, p, n parameters which are here inferred by fitting the wind speed and diffusivity profiles over a height range 0.2-20 m while in Foken and Meixner (2001) it was computed by forcing the profiles at a reference height. The FIDES model was shown to behave similarly to a Lagrangian Stochastic model in Loubet et al. (2017).

For the concentration measurements, Alpha passive air samplers (Tang et al., 2001) were used. These samplers are small hollow plastic tubes (27 mm ID) with a PTFE membrane which allows air to pass through. Inside there is a layer of filter paper coated with citric acid which traps atmospheric NH_3 and holds it in place within the sampler. This method enabled us to measure cumulative NH_3 concentrations at a fixed point, integrated over a certain period of time (t) of several hours or days. To observe χ_{meas}, duplicate samplers were positioned at the centre of the 16 treatment plots (20 by 20 m) at heights of 30 and 50 cm. In order to measure $\chi_{bgd,}$ samplers were installed in triplicate at the four edges of the experimental grid, 30 m away from the plots. Samplers were placed immediately before fertilisation and removed/replaced 0.25, 1, 2, 3, 7 and 14 days after fertilisation. Samplers were stored at 4 °C after collection before extraction by deionised water and analysis using Ammonia Flow Injection Analysis (AMFIA, CEH Edinburgh, UK). Due to logistical constraints, we were limited in the number of measurements we could make using the FIDES method. Based on the extensive experience of the researchers in the field of NH_3 flux measurements, and numerous studies of NH_3 emissions (e.g. Gericke et al., 2011; Sanz-Cobena et al., 2011; Suter et al., 2013) we decided to measure for a period of two weeks, which would allow us to capture the vast majority of any cumulative emissions associated with the fertiliser event, which typically last only several days.

2.5. Soil Measurements

Soil cores were sampled from a distance of approximately 2 m from the static chambers (within the appropriate experimental plot) each time N_2O flux measurements were made. Cores were 3 cm in diameter and 10 cm in depth. Samples were frozen immediately after collection and stored at -18 °C until further processing up to three months later. Potassium Chloride (KCl) solution (50 ml, 1 mol L^{-1}) was used to extract Nr (in the form of NH_4^+ and NO_3^-) from the samples (15 g, wet soil). Having added the 1 M KCl solution to the samples, they were subsequently mixed on an orbital shaker for 60 mins before the solution was filtered using 2.5 µm filter paper (Fisherbrand, US) and stored at -18 °C for

analysis up to three months later. A further 10 g of mixed soil was dried to provide the dry soil ratio of each soil sample.

Concentrations of NH_4^+ and NO_3^- in the soil extracts were measured using a SEAL AQ2 discrete analyser (SEAL Analytical, US) fitted with a cadmium coil. The widely used phenol-hypochlorite (for NH_4^+) and sulfanilamide (NO_2^- & NO_3^- after cadmium coil reduction) methods were used to provide the relevant colorimetry reactions. Concentrations of NH_4^+ and NO_3^- in soil was then calculated based on the mass of dry soil in the initial KCl extraction.

2.6. Meteorological data

Long term meteorological and soil measurements were recorded at the permanent Easter Bush measurement station, which was situated at the edge of the Engineer's Field. This station provided measurements of air temperature (1.8 m), soil temperature (0.3 m depth) and rainfall (tipping bucket) at 30 min intervals throughout the measurement campaigns (Fig. 1).

3. Results

3.1. Crop Yield, NUE and Quality

Although rainfall and temperature was similar during both years of measurement, crop yields for all treatments were substantially larger in the 2016 field plots (5.5 t ha^{-1}) than the 2017 field plots (1.48 t ha^{-1}) (Table 2), indicating that the Engineer's field was the more productive of the two experimental areas regardless of fertiliser application or meteorological conditions. There was reasonably large variation in yield measurements from the harvests in both fields, and in some cases (October 2016) the effect of the addition of fertiliser (i.e. dry control yields subtracted from dry yields of fertilised plots) appeared to have a negative effect on yield (although these values fall well within the large uncertainty range around zero). The most efficient fertiliser overall was ammonium nitrate (Nitram), increasing yields (after subtraction of the control) on average by 1.05 ± 0.61 t ha^{-1} with a mean NUE of 35.5 %. Urea and inhibitor coated urea increased yields by an average of 0.66 ± 0.62 and 0.69 ± 0.73 t ha^{-1}, respectively. Nitram treatment was found to increase yields significantly (p-value < 0.05) when compared to the urea fertilisers. The treated urea had a slightly higher average NUE than the untreated urea (24.6 and 20.7 %, respectively), but this difference was not statistically significant (p-value = 0.91).

Crude protein (and therefore nitrogen) content of the fertilised plots (154 g kg^{-1}) was typically higher than that of the control plots (102 g kg^{-1}) for all fertiliser treatments; however, there were no outstanding differences between the treatment types. Differences in metabolizable Energy (Grass ME), modified acid detergent (MAD) and decimal reduction time (D value) between the fertiliser treatments were also small, and varied more between the two field sites than the fertiliser types 2. These indicators of digestibility and energy content are commonly used to indicate the quality of the silage grass for

307 animal feed and our study suggests that there was no significant differences between the feedstock
308 grown using the different fertilisers.

309 *3.2. N_2O Fluxes*

310 N_2O fluxes from the chambers ranged from -0.39 to 24.47 nmol m^{-2} s^{-1} and showed a log-normal spatial
311 distribution. The majority of flux measurements were close to zero with 81 % below 1 nmol m^{-2} s^{-1} in
312 magnitude (Fig. 2). Observed fluxes increased in magnitude from the plots treated with Nitram
313 immediately after fertilisation, typically peaking within a week of the Nr application. Fluxes also
314 increased after the urea and inhibitor coated urea applications, although the timing of the peaks in
315 these emissions were more variable than those observed from the Nitram plots.

316 Cumulative flux estimations of N_2O from the individual fertilisation events have a typical large
317 relative uncertainty, due to the difficulty in extrapolating measurement data both spatially and
318 temporally from small data sets. In this study we have chosen to calculate cumulative fluxes using the
319 Bayesian model outlined in equations 2 to 5 rather than the trapezoidal method (linear interpolation
320 between mean values) in order to better represent this uncertainty (Levy et al., 2017). Regardless of
321 the large associated uncertainties in cumulative flux estimates, our measurements show that the
322 Nitram fertiliser results in significantly larger N_2O emissions when compared to the urea and inhibitor
323 coated urea applications of the same quantity of Nr (p-value < 0.05) (Table 3). In four of the five events,
324 Nitram was the highest N_2O emitting fertilizer of the treatments after 30 days (minus background from
325 control plots) with a mean EF between replicates of 0.76 ± 0.63 % (Table 3). Emissions from the urea
326 and the inhibitor treated urea were comparable in magnitude, 0.29 ± 0.27 % and 0.36 ± 0.15 % of the
327 applied Nr, respectively.

328 *3.3. NH_3 Fluxes*

329 Ammonia fluxes were only measured during the 3 fertilisation events in 2017. The majority of the NH_3
330 emissions occurred between 0 and 5 days after fertiliser was applied, and emissions beyond 7 days after
331 fertiliser application were largely negligible. Emissions of NH_3 from the plots varied widely with
332 cumulative flux values from individual plots ranging from -1.8 to 13.1 kg N ha^{-1} at the end of the 14 day
333 measurement period (Fig. 3 & Table 4). Emissions from the plots treated with urea fertiliser were
334 consistently higher than those of the other treatments after fertiliser applications. Mean cumulative
335 emissions for each of the fertiliser types after all three fertilisation events (n= 12) were -0.74, -0.95,
336 10.83 and 0.42 kg N ha^{-1} for the control, Nitram, urea and inhibitor treated urea, respectively.

337 Differences in NH_3 from individual plots was typically larger than an order of magnitude of the
338 mean value of the grouped treatments. As the control plots represent a near zero influence situation,
339 the mean flux observed from the control plots for each event were subtracted from the fluxes

associated from the treatment measurements. Based on this, emissions from the urea treated plots (mean of 16.5 ± 5.0 % of applied N) were considerably higher than each of the other treatments (-0.3 ± 1.8 % and 1.66 ± 2.0 % for Nitram and the inhibitor coated urea, respectively). Fluxes measured from the Nitram plots were not significantly different to those from the control plots (p-value = 0.42), but emissions from the inhibitor coated urea were (p-value < 0.1).

3.4. Soil Chemistry

As shown in Fig. 4, concentrations of NH_4^+ varied by several orders of magnitude, with individual measurements ranging from 1.3 to 1525 mg of nitrogen per kg of soil sampled (mg kg^{-1}). Concentrations of NH_4^+ were consistently low in the experimental plots before fertiliser application; with the exception of the first fertiliser event in 2016 where elevated Nr was observed in the control plots, possibly due to residues from sheep grazing in the field close to one month before the experiment began. Concentrations of NH_4^+ typically rose in magnitude for several days after fertiliser application before returning to pre-fertiliser magnitudes by the end of the measurement period. Concentrations of NH_4^+ in soils treated with urea and inhibitor coated urea were typically higher than those that received Nitram fertiliser. During the third fertiliser event (13/03/17) there was a clear delay in the rate at which urea was hydrolysed into NH_4^+ in the soil (Fig. 4). This phenomenon was not observed during the other events.

Concentrations of NO_3^- followed a log-normal distribution in a similar fashion to the NH_4^+ concentrations. Nr in the form of NO_3^- was typically lower than that of $NH_4^+$with measured values ranging from 0.05 to 165 mg kg^{-1}. As with NH_4^+, NO_3^- concentrations in the experimental plots were near zero before fertiliser application, with the exception of the first event. After Nitram application, NO_3^- concentrations typically rose then decreased in concentration with time.

4. Discussion

The yield and nitrogen uptake of the silage crop varied widely across the plots and seasons during the experiment. The quantity of the applied fertiliser that was consumed by the crops ranged from a maximum of 66 % to a negative value of -16 % compared with the adjacent control plots. As there were only small differences between the total N content of the crop for the three different fertiliser types, the percentage of applied N that was present in the harvest from the plots scales closely with the overall dry yield. In this respect, the Nitram treated plots have the highest NUE of the three treatments with a mean NUE of 35 ± 19 % when compared to urea (21 ± 15 %) and the inhibitor treated urea (24 ± 20 %).

The perceived negative effect of fertiliser application during the 2016 trials may have been influenced by a considerably large amount of clover that had begun to grow in the plots by late spring. The nitrogen fixing properties of the clover may have had some impact on the results of the experiment, although not atypical of grazed grasslands (Marriott, 1988). We speculate that the prior grazing of the sheep is also likely to have resulted in the residues of animal waste in the 2016 plots, which would explain the higher than expected yields and Nr in the soil measurements in these plots (Cowan et al., 2015). Although unintentional, the presence of these two factors sheds some light into the importance of N-fixation and animal waste in grazed fields which often receive similar applications of N fertiliser as arable crops. The 2016 plots in our study show that when there is a large amount of Nr already present in the soils, the application of further Nr can have negligible effect on yield, while still contributing to N pollution. This highlights the future potential of precision farming methods which could take into account the spatial variability of Nr already present in the field and attempt to improve NUE by better managing where fertiliser is required, and where it is not (Auernhammer, 2001; Kindred et al., 2017).

The 2017 plots did not appear to be influenced by clover growth or residues of animal waste after visual inspection, and subsequently the observed NUE was more comparable to values considered typical under the conditions (Raun and Johnson 1999). Overall, the Nitram application resulted in the highest average yield, but there was little difference in yield observed between the urea and inhibitor coated urea in this study. The crude protein content of the silage harvests varied largely between events, but the treatment effect was small and inconsistent. Differences in metabolizable Energy (Grass ME), modified acid detergent (MAD) and decimal reduction time (D value) between the fertiliser treatments were also small, with little variation observed between the events and the treatment types.

Emissions of N_2O were higher from the plots treated with Nitram fertiliser than from the other treatments. This observation is consistent with previous research which has identified Nitram as a higher emitter than urea fertiliser (DEFRA, 2006; Harty et al., 2016). Previous studies highlight a potential for pollution swapping with nitrification inhibitor treated urea (typically dicyandiamide, a.k.a. DCD), suggesting that by reducing the rate of conversion of NH_4^+ to NO_3^- in soils that NH_3 emissions are increased (Lam et al., 2016; Zaman et al., 2009). Elevated N_2O and NH_3 emissions have been observed

on occasion after the use of nitrification inhibitors (Scheer et al., 2017; Zaman et al., 2009); however reductions in both have also been observed (Di et al., 2006; Misselbrook et al., 2014) . This should not be the case for urease inhibitors as it slows the release of Nr from the applied fertiliser, thus reducing the potential of N_2O and NH_3 emissions. Previous studies have shown that the use of urease inhibitors can significantly reduce N_2O emissions (Singh et al., 2013; Zaman et al., 2009). In this study, emissions from the inhibitor treated urea were slightly larger overall compared to the urea; however, the treatments behaved similarly throughout the experiment and the differences observed in this study were not statistically significant (p-value = 0.42). The emissions of N_2O were not found to correlate well with any of the measured environmental variables such as rainfall or temperature, which is not uncommon. The wide variety of complex interacting conditions that influence microbial processes often prevent predictive modelling and correlation with environmental variables (Butterbach-Bahl et al., 2013).

Emissions of NH_3 calculated using the FIDES method were consistently largest from the plots treated with urea fertiliser (mean EF of 16.5 % of applied Nr). The emissions from the Nitram plots were not significantly different from the control plots, suggesting that emissions were negligible from this treatment. These observations agree with previous studies in that urea treatments are expected to lose a large fraction of Nr as NH_3 emissions (Sommer et al., 2004) while Nitram treatments do not (DEFRA, 2005). The urease inhibitor appears to have significantly reduced NH_3 losses from the inhibitor coated urea plots, reducing emissions of NH_3 by approximately 90 % when compared to the untreated urea. This effect has been observed in other similar studies when applying a urease inhibitor to urea fertiliser (Li et al., 2015: Rawluk et al., 2001). The large reduction in NH_3 volatilisation and lack of yield response does raise the question of the fate of the Nr in the urease treated urea plots.

After the N content of the crop, the N content of the soil and emissions of N_2O and NH_3 are taken into account, the majority (> 55 %) of applied Nr in the experiments remains unaccounted for by the time of harvest. Typically, Nr in the form of NH_4^+ and NO_3^- in the top 10 cm of soil has returned to concentrations on par with the control plots by harvest. When compared to the control plots, the remaining extractable Nr in the top 10 cm of the fertiliser treated plots at time of harvest accounted for less than 1 % of the applied nitrogen in all cases in this study. Other known pathways for large losses of Nr from agricultural soils include the leaching of NO_3^- into deeper soils and water systems, uptake of Nr into root systems, and microbial nitrification and denitrification which produces nitric oxide (NO) and gaseous nitrogen (N_2). Leaching can account for 2 - 33 % of applied Nr (Riley et al. 2001; Sebilo et al. 2013; Skinner et al. 1997), root systems may consume Nr in the same order of magnitude as the harvested shoots (Watson, 1987) and microbial emissions of NO and N_2 can account for Nr losses of an order of magnitude higher than N_2O when water filled pore space (WFPS) is particularly low (< 40 %) or high (> 80 %) (Davidson 1993; Weier 1993). All of these potential processes may account for a significant

fraction of the unaccounted Nr applied to the plots in this experiment and measurements should be included in future studies when logistically possible.

5. Conclusions

Large variations in crop yield measurements show that none of the fertiliser types used in this study consistently outperforms the others in terms of NUE. However, of the three fertilisers used, Nitram performed better on average than the urea compounds in this experiment with an average NUE of 35% when compared to urea (21 %) and the inhibitor treated urea (24 %). This study supports previous research which suggests that Nitram is the largest emitter of N_2O (0.76 % of applied Nr) and that urea fertiliser is the largest emitter of NH_3 (16.5 % of applied Nr) when the mineral fertilisers are compared. The use of the urease inhibitor resulted in a considerably large reduction in NH_3 losses from the urea fertiliser (decrease of 90 %) without significantly increasing emissions of N_2O; however, yields were statistically the same. The results of this study suggest that urease inhibitors, such as Agrotain®, can play an important role in mitigating Nr-related air pollution. However the agronomic benefits to the farmer appear to be negligible. With the higher costs of urea coated with urease inhibitors, there is no incentive for farmers to switch to these more environmentally friendly compounds. Our experiments are short term only. There certainly is a need for more long-term studies covering different climate zones, crop types and soil properties to investigate the economic and environmental benefits of switching from the preferred ammonium nitrate fertilisers in the UK to urea treated with urease inhibitors, or even double inhibition using nitrification and urease inhibitors.

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7. Author Contribution

N. Cowan managed the fieldwork, carried out data analysis and wrote the manuscript. P. Levy contributed to the Bayesian statistics and was involved in the writing of the manuscript. A. Moring, B. Loubet and P. Voylokov worked on the data analysis and the FIDES method. I. Simmons, C. Bache, A. Stephens, J. Marinheiro, J. Brichet, L. Song, A. Pickard, C. McNeill, R. McDonald and J. Maire were involved in the fieldwork and laboratory analysis stages of the research. M. Sutton provided guidance on the measurement aspects of ammonia and helped develop the data analysis. U. Skiba is the primary

investigator of the Cinag project at CEH Edinburgh, managing the project overall, contributing to all aspects of the research and the writing of the manuscript.

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652 **Table 1** Management of experimental plots over five fertilization events at Easter Bush Farm, 2016 &
653 2017. 70 Kg-N ha-1 was applied each time.

Field	Event	N Application	Harvest	No. of Plots	Plot Size	Days of Crop Growth
Engineers	1	13/06/2016	15/07/2016	16	16 m^2	32
Engineers	2	27/07/2016	03/10/2016	16	16 m^2	68
Upper Joiner	1	13/03/2017	25/05/2017	16	80 m^2	73
Upper Joiner	2	12/06/2017	19/07/2017	16	80 m^2	37
Upper Joiner	3	07/08/2017	15/09/2017	16	80 m^2	39

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Table 2 Crop quality measurements of sub-samples taken from harvests of all experimental treatment plots. Mean values and standard deviation of samples are provided (n = 4 replicates). Effect of N addition is reported as the additional dry matter (DM) harvested compared to the control plots. The total N content of the dry matter and NUE for each event are presented.

Event	Treatment	Dry Yield (t ha^{-1})	Effect of N Addition (t ha^{-1} DM)	Crude Protein (g kg^{-1})	N content (g kg^{-1})	NUE (%)
2016						
1	Control	6.7 ± 0.8		72.2 ± 6.2	11.6 ± 1	
1	Nitram	8.5 ± 0.5	1.8 ± 0.9	95.2 ± 15.3	15.2 ± 2.5	39.1
1	Urea	8 ± 1.2	1.3 ± 1.4	93.8 ± 21.5	15 ± 3.4	27.9
1	Urea & Inhibitor	7.9 ± 1	1.2 ± 1.3	111.8 ± 12.8	17.9 ± 2.1	30.7
2	Control	3.4 ± 1.1		120.8 ± 8.1	19.3 ± 1.3	
2	Nitram	3.8 ± 0.2	0.4 ± 1.1	122 ± 12.1	19.5 ± 1.9	11.1
2	Urea	2.9 ± 0.4	-0.5 ± 1.2	116.2 ± 28.3	18.6 ± 4.5	-13.3
2	Urea & Inhibitor	2.8 ± 0.8	-0.6 ± 1.3	117.8 ± 14.8	18.8 ± 2.4	-16.1
2017						
1	Control	0.6 ± 0.2		78.9 ± 3.8	12.6 ± 0.6	
1	Nitram	2.4 ± 0.8	1.8 ± 0.8	160.5 ± 37.4	25.7 ± 6	66.1
1	Urea	1.6 ± 0.2	1 ± 0.3	102.2 ± 5.4	16.4 ± 0.9	23.4
1	Urea & Inhibitor	2.1 ± 0.4	1.6 ± 0.4	130.9 ± 40.2	20.9 ± 6.4	47.8
2	Control	1.1 ± 0.3		94.8 ± 9	15.2 ± 1.4	
2	Nitram	2 ± 0.2	0.9 ± 0.3	191.8 ± 35.5	30.7 ± 5.7	27.6
2	Urea	2.1 ± 0.3	1 ± 0.4	165 ± 23.8	26.4 ± 3.8	26.4
2	Urea & Inhibitor	1.8 ± 0.3	0.8 ± 0.4	173.8 ± 9	27.8 ± 1.4	22.2
3	Control	0.7 ± 0.3		141 ± 13	22.6 ± 2.1	
3	Nitram	1 ± 0.4	0.4 ± 0.5	236.8 ± 31.9	37.9 ± 5.1	15.2
3	Urea	1.2 ± 0.6	0.5 ± 0.7	241.8 ± 17.9	38.7 ± 2.9	19.4
3	Urea & Inhibitor	1.1 ± 0.2	0.5 ± 0.4	251.8 ± 14.9	40.3 ± 2.4	20.2

662 **Table 3** Cumulative N_2O fluxes estimated using the Bayesian interpolation method over a 30 day period
663 after fertilizer applications (70 kg N ha^{-1}) at two intensively managed grassland sites. Values presented
664 represent 4 plots (n = 4) per event at each field site. Emission factors (EF) account for the effect of N
665 application after the measured background flux has been deducted from cumulative totals.

Event	Fertiliser Type	Background Flux (kg N ha^{-1})	Cumulative Flux (kg N ha^{-1})	95 % C.I. min	95 % C.I. max	Flux Minus Background (kg N ha^{-1})	EF (%)
2016							
1	Nitram	0.25	1.59	1.02	2.86	1.34	1.92
1	Urea	0.25	0.52	0.37	0.78	0.27	0.38
1	Urea & Inhibitor	0.25	0.54	0.37	0.90	0.28	0.41
2	Nitram	0.19	0.45	0.32	0.68	0.25	0.36
2	Urea	0.19	0.30	0.24	0.40	0.11	0.15
2	Urea & Inhibitor	0.19	0.29	0.23	0.40	0.10	0.14
2017							
1	Nitram	0.92	1.39	0.97	2.26	0.48	0.68
1	Urea	0.92	0.99	0.72	1.48	0.07	0.10
1	Urea & Inhibitor	0.92	1.33	0.87	2.46	0.41	0.58
2	Nitram	0.51	0.50	0.39	0.67	-0.01	-0.01
2	Urea	0.51	1.06	0.64	2.10	0.55	0.79
2	Urea & Inhibitor	0.51	0.67	0.50	0.97	0.17	0.24
3	Nitram	0.93	1.53	1.08	2.34	0.60	0.85
3	Urea	0.93	0.97	0.77	1.27	0.04	0.05
3	Urea & Inhibitor	0.93	1.22	0.89	1.83	0.29	0.41

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668 **Table 4** Cumulative fluxes of NH_3 estimated the FIDES method over a 14 day period after fertilizer
669 applications (70 kg N ha^{-1}) at the Upper Joiner grassland. Values presented represent 4 plots (n = 4) per
670 event at each field site. Emission factors account for the effect of N application after the measured
671 background flux has been deducted from cumulative totals. The 95 % C.I. is calculated using the least
672 squares method to combine the standard error between the replicates for each treatment.

Event	Fertiliser Type	Cumulative Flux (kg N ha^{-1})	Std. Error in Cumulative Flux (kg N ha^{-1})	Flux Minus Background (kg N ha^{-1})	95 % C.I. (kg N ha^{-1})	EF (%)
1	Control	0.36	1.19			
1	Nitram	-0.83	1.28	-1.19	1.75	-1.70
1	Urea	11.37	1.76	11.01	2.13	15.73
1	Urea & Inhibitor	0.65	1.36	0.29	1.81	0.41
2	Control	-0.75	0.46			
2	Nitram	-1.19	1.05	-0.44	1.14	-0.63
2	Urea	8.04	0.99	8.79	1.09	12.56
2	Urea & Inhibitor	-0.16	0.88	0.60	0.99	0.86
3	Control	-1.81	1.77			
3	Nitram	-0.82	3.17	0.99	3.63	1.42
3	Urea	13.09	3.34	14.90	3.78	21.29
3	Urea & Inhibitor	0.78	1.81	2.60	2.54	3.71

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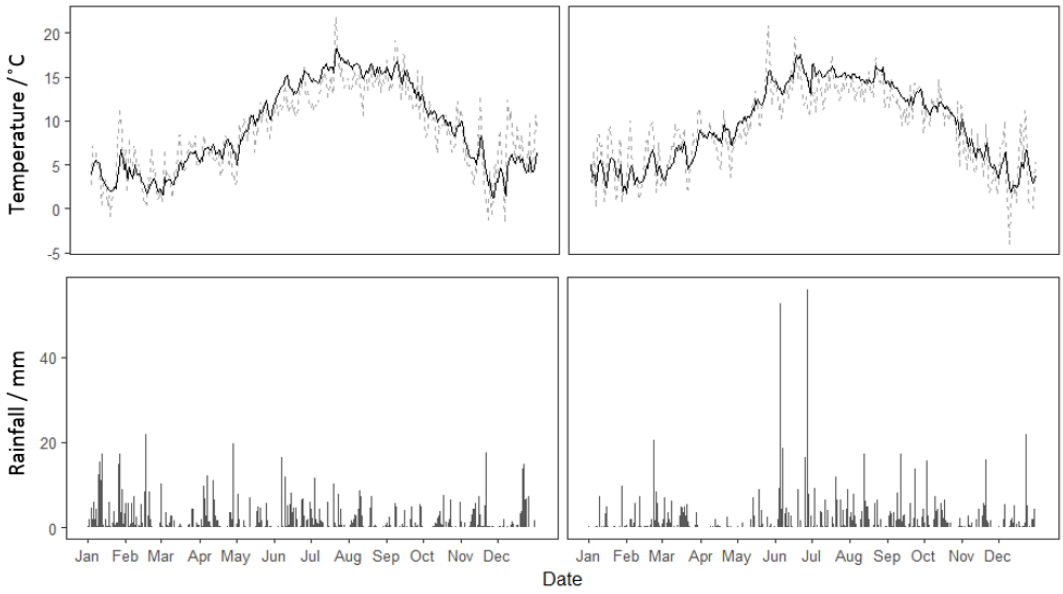

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676 **Figure 1** Meteorological data recorded at Easter Bush Farm over 2016 (left) and 2017 (right). Daily mean
677 soil temperature (black) and air temperature (grey) and daily cumulative rainfall are presented.

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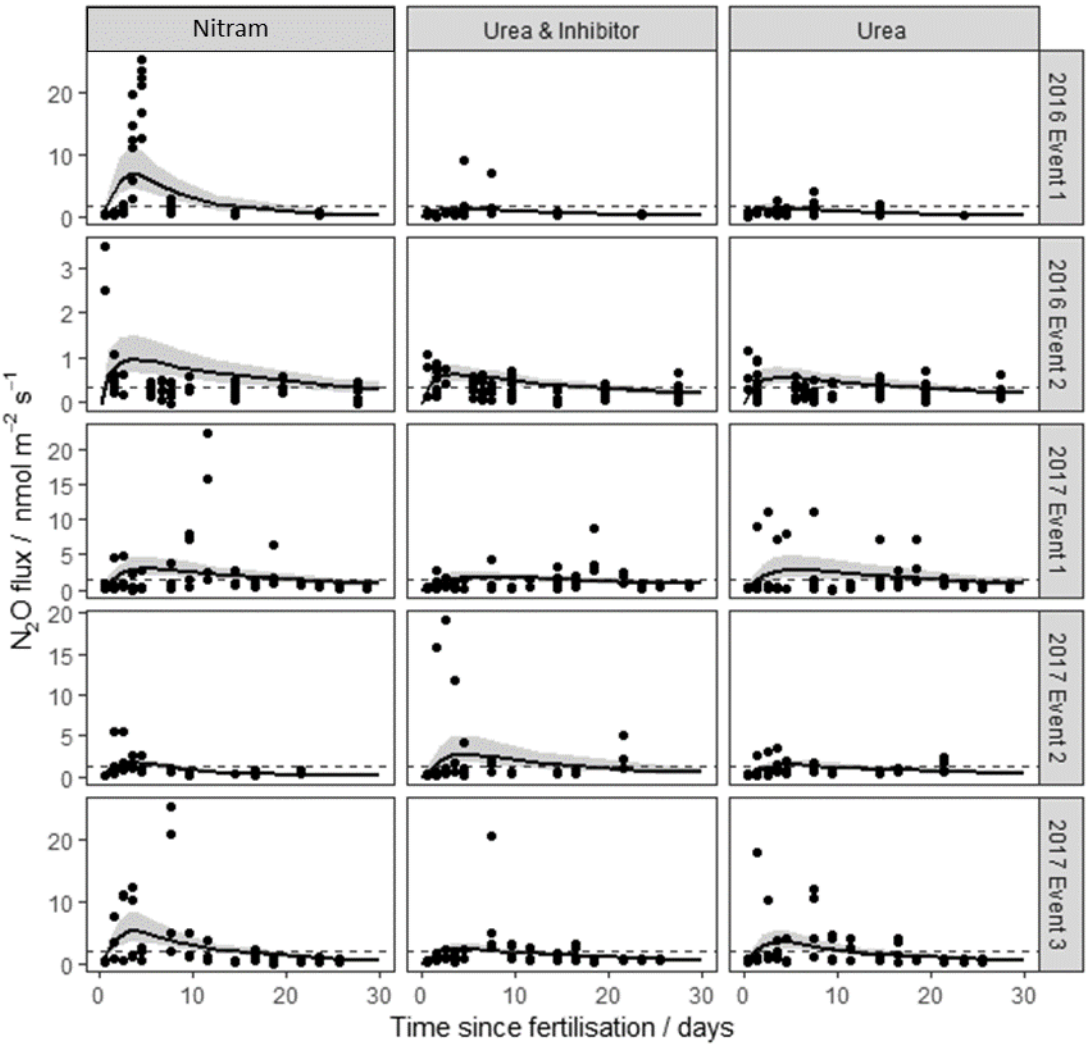

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681 **Figure 2** N_2O fluxes following fertilisation of the Engineer's field in 2016 and Upper Joiner field in 2017.
682 Fertiliser was applied at t = 0 days, and the measurements lasted up to 30 days for each event. The log-
683 normal model was used to estimate cumulative N_2O fluxes. The 95 % credible intervals of the posterior
684 predictions are shown as the shaded area. Mean background fluxes from control plots are included for
685 each event (dashed line).

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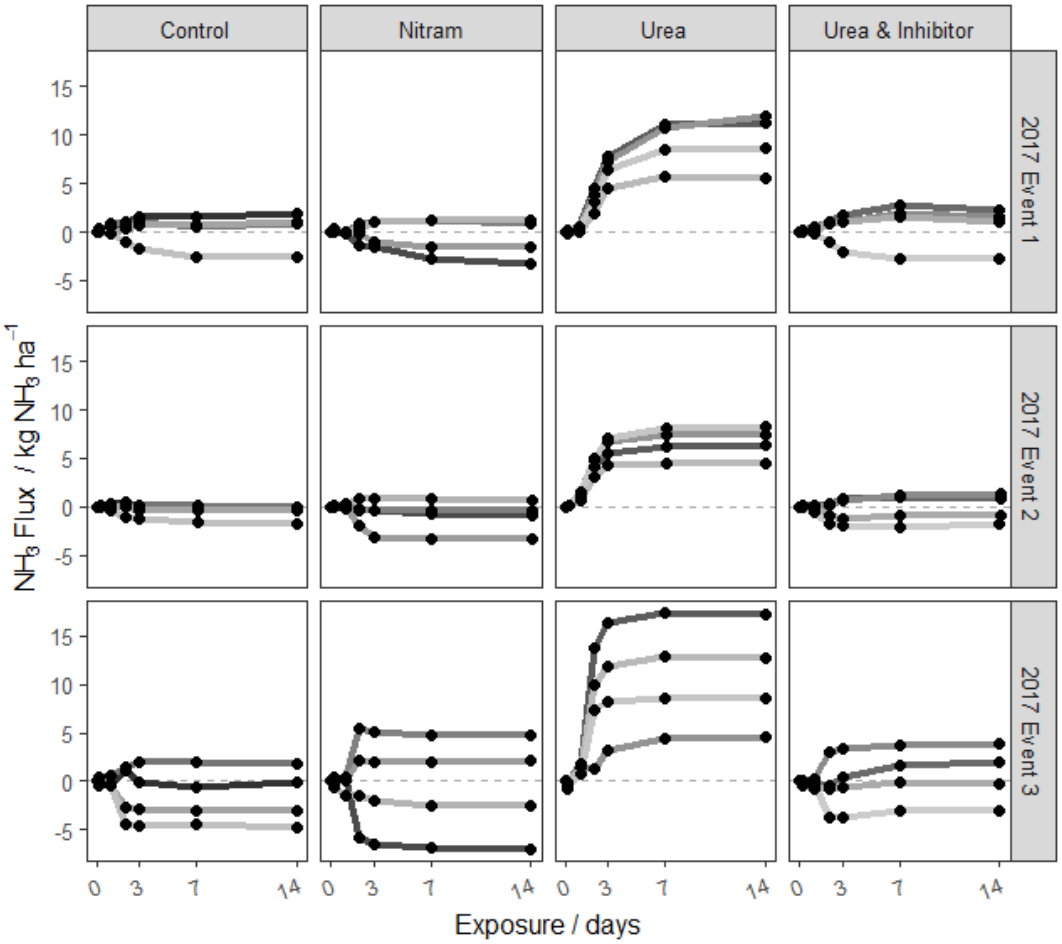

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689 **Figure 3** Cumulative fluxes from each of the experimental plots during three fertilisation events
690 measured using the FIDES method (2017). Each shaded line represents one of the four plots replicated
691 for each treatment.

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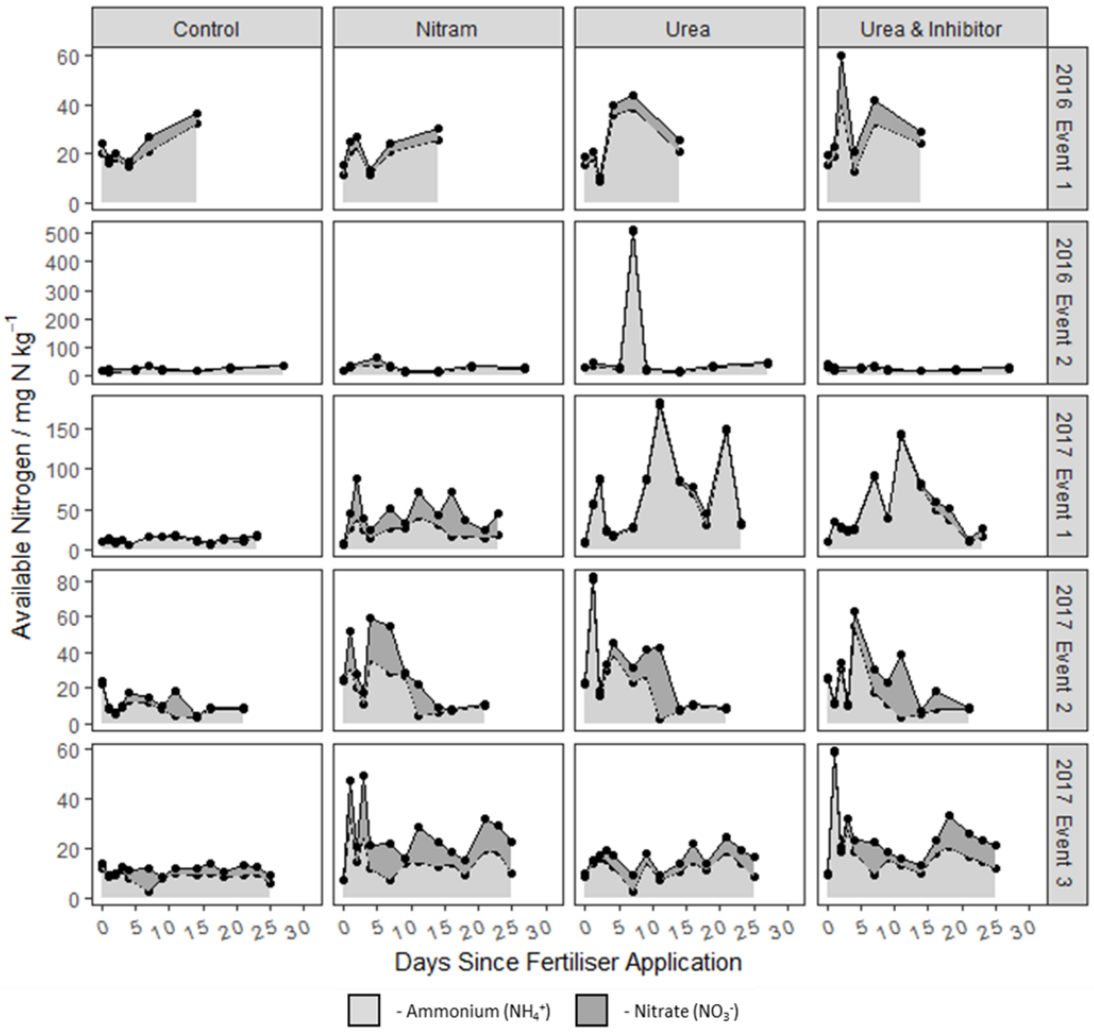

693

694 **Figure 4** Median available nitrogen concentrations measured in tandem with N_2O chamber

695 measurements after fertilisation events.

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