

1 **Nitrogen use efficiency and N₂O and NH₃ losses attributed to three fertiliser types applied to an**
2 **intensively managed silage crop**

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19

20 **Abstract**

21 Three different nitrogen (N) fertilizer types, ammonium nitrate, urea and urea coated with a urease
22 inhibitor (Agrotain®), were applied at standard rates (70 kg N ha⁻¹) to experimental plots in a typical and
23 intensively managed grassland area at Easter Bush Farm Estate (Scotland). The nitrogen use efficiency
24 of the fertilisers was investigated as well as nitrogen losses in the form of nitrous oxide fluxes (N₂O) and
25 ammonia (NH₃) during fertilisation events in the 2016 and 2017 growing seasons. Nitrous oxide was
26 measured by the standard static chamber technique and analysed using Bayesian statistics. Ammonia
27 was measured using passive samplers combined with the FIDES inverse dispersion model. On average,
28 fertilisation with ammonium nitrate supported largest yields and had the highest nitrogen use
29 efficiency, but as large spatial and seasonal variation persisted across the plots, yield differences
30 between the three fertilizer types and zero N control were not consistent. Overall, ammonium nitrate
31 treatment was found to increase yields significantly (p-value < 0.05) when compared to the urea
32 fertilisers used in this study. Ammonium nitrate was the largest emitter of N₂O (0.76 % of applied N)
33 and the urea was the largest emitter of NH₃ (16.5 % of applied N). Urea coated with a urease inhibitor
34 did not significantly increase yields when compared to uncoated urea; however, ammonia emissions
35 were only 10 % of the magnitude measured for the uncoated urea, and N₂O emissions were only 47 %
36 of the magnitude of those measured for ammonium nitrate fertiliser. This study suggests that urea
37 coated with a urease inhibitor is environmentally the best choice in regards to nitrogen pollution, but
38 because of its larger cost and lack of agronomic benefits, it is not economically attractive when
39 compared to ammonium nitrate.

40

41 **1. Introduction**

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

53 After fertiliser application, the resulting volatilization of NH_3 , especially from urea, will often
54 contaminate the surrounding environment with deposition of Nr, in some cases causing significant
55 damage to fragile biodiversities by increasing nitrogen loading (Phoenix et al. 2006). Fluxes of NH_3 also
56 contribute to an increase of particulate matter ($\text{PM}_{2.5}$) in the atmosphere which has negative
57 implications for human health (Paulot and Jacob 2014). Agricultural sources contribute an estimated
58 60 % of global anthropogenic N_2O emissions (Syakila and Kroeze 2011), primarily due to increasing the
59 quantity of Nr in soils and aquatic systems in which N_2O is released as a byproduct of the microbial
60 processes of nitrification and denitrification (Davidson et al. 2000). N_2O is a potent greenhouse gas as
61 well as the most significant contributor to global stratospheric ozone depletion (Ravishankara et al.,
62 2009) which doubly increases the incentive to mitigate these emissions.

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

78 Several methods have been tested to slow down the release of Nr from synthetic fertilisers. In
79 its simplest form, this can be achieved by increasing the particle size of the applied fertilizer pellets
80 (Azeem et al., 2014; Shamsudin et al., 2014). More complicated methods of Nr inhibition come in the
81 form of microbial inhibitors which directly target and slow a specific biological pathway (Abalos et al.,
82 2014; Modolo et al., 2015). Synthetic fertilisers (typically urea) coated with chemical inhibitors that
83 target urease hydrolysis and microbial nitrification are already commercially available.

84 Microbial inhibitors have been shown to reduce Nr losses for both N₂O and NH₃ under
85 laboratory conditions and in field trials, but with varying success (Sanz-Cobena et al., 2016; Ni et al.,
86 2014; Singh et al., 2013; Rose et al., 2017; Ruser and Schulz 2015). Although there are positive studies
87 which promote the pollution reducing capabilities of these chemicals (Misselbrook et al., 2014), some
88 questions remain over the overall effectiveness of the inhibitors which face claims that reduction of
89 one form of Nr pollution may increase another. This is most commonly observed for nitrification
90 inhibitors in which the slowing on the conversion of NH₄⁺ to NO₃⁻ in soils results in a decrease in N₂O at
91 the expense of an increase in NH₃ volatilisation (Lam et al., 2016; Zaman et al., 2009). In theory, the use
92 of a urease inhibitor should reduce both the emission of NH₃ by reducing the rate at which urea is
93 converted to NH₄⁺ in soils, thus limiting available nitrogen in all forms. This may however, limit the rate
94 at which crops also receive Nr and reduce yields. The use of inhibitors in farming remains uncommon,
95 mostly due to a reluctance to change to an uncertain practice, compounded by the drawback that
96 treated fertilisers are typically more expensive than traditionally used products. Further work using
97 specific products in different environments is needed to supply evidence that will provide the
98 agricultural community with the confidence to make the changes required to meet future NUE
99 demands globally.

100 This study aims to specifically investigate the effect of the Agrotain® urease inhibitor (Koch,
101 KS, USA) on a typical grassland silage crop in Scotland, comparing it with the two most commonly used
102 synthetic nitrogen fertilisers: Ammonium nitrate (Nitram®) and urea. Grasslands account for
103 approximately 60% of agricultural land use in the UK (approximately 74,000 km²) to which an estimated
104 120 kt of ammonium nitrate and 26 kt of urea are applied annually (BSFP, 2017). The results presented
105 in this study are intended to represent to some extent this large coverage of agricultural land in the UK
106 to which urease inhibitors may be applied in the future.

107 In this study we aim to:

- 108 • Compare the nitrogen use efficiency of equivalent applications of pellet fertilisers in the form of
109 ammonium nitrate (Nitram), urea and urea with a urease inhibitor (the percentage of applied
110 nitrogen fertiliser that is converted into plant matter as a result of increased crop growth).
- 111 • Investigate differences in crop quality and yield as a result of the fertilisers applied.
- 112 • Quantify gaseous losses of nitrogen from the fertiliser types in the form of NH₃ and N₂O.

113

114 **2. Materials and methods**

115 *2.1. Experimental Design*

116 Fieldwork was carried out between May 2016 and September 2017. During this time, five applications
117 of three different nitrogen fertiliser types were added to a grid of experimental plots (including a
118 control) in intensively managed silage grassland fields (*Lolium perenne L.*) at Easter Bush Farm
119 (Midlothian, UK, 55°51'57.4"N 3°12'29.3"W). The three fertiliser types used in the experiment were
120 ammonium nitrate pellets (Nitram, $\text{NH}_4^+\text{NO}_3^-$), urea pellets, and urea pellets with a coating of powdered
121 urease inhibitor (N-(n-butyl) thiophosphoric acid Triamide; Agrotain®). In 2016, fertiliser was applied
122 twice to experimental plots known as the Engineers Field (Cowan et al., 2016). In 2017, fertiliser was
123 applied three times to experimental plots in an adjacent similarly managed field (known as the Upper
124 Joiner field).

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

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

144 *2.2. Crop Yield and Quality Measurements*

145 Each of the plots was harvested and above-ground biomass was dried at $60 \text{ }^\circ\text{C}$ for 24 hours and both
146 wet and dry weights were recorded. For the smaller 2016 plots, a 1 m^2 section of each plot was
147 harvested manually using shears (i.e. 1 sample per plot). For the larger 2017 plots, a small harvester

148 with onboard weighing capabilities (Haldrup F-55) was able to harvest an area of 30 m² from which
149 yield data were obtained. After wet yield was recorded, subsamples were taken from each of the
150 individual plots for further analysis (at SRUC Analytical Services, Midlothian, UK). The dry matter
151 content, metabolizable energy (ME), crude protein, modified acid detergent (MAD), decimal reduction
152 time (D value), total carbon and total nitrogen contents were all analysed from the subsamples.

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

161 2.3. N₂O Flux Measurements

162 Measurements of N₂O fluxes were taken for both 2016 and 2017 experiments using the static chamber
163 approach. The chambers consisted of a cylindrical polyvinyl chloride (PVC) plastic pipe of 38 cm inner
164 diameter (ID) and 22 cm height fitted with a sealed lid and a flange at the base. The chambers were
165 placed onto a plastic flanged collar that had been inserted several centimeters into the soil (on average
166 5 cm) to form a seal in the soil. A layer of draught sealant material held in place by four strong gripping
167 clips formed an airtight seal between the chamber and the collar for the duration of the flux
168 measurement. Chambers were closed for 60 min, during which time four gas samples were collected
169 via a syringe and a three-way tap fitted to the lid, at t = 0, 20, 40 and 60 minutes. Gas samples were
170 stored in 20 ml glass vials which were flushed with 100 ml of air from the syringe using a double needle.
171 Samples were analysed using gas chromatography (7890B GC system fitted with an electron capture
172 detector, Agilent Technologies, UK), with a limit of detection of 7 ppb (Drewer et al., 2017).
173 Measurements were carried out daily for two weeks after fertilisation, then every second day for a
174 further two to four weeks. Measurements were made only on working days (Monday to Friday)
175 between 09:00 and 15:00 GMT.

176 Fluxes were calculated as:

$$177 \quad F = \frac{dC}{dt} \cdot \frac{\rho V}{A} \quad (\text{Eq. 1})$$

178 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
179 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
180 of the chamber in cubic meters and A is the ground area enclosed by the chamber in square meters.

181 Cumulative fluxes over the experimental periods (30 days) were calculated using a Bayesian
 182 approach, taking into account the log-normal distribution of spatial samples and the lognormal peak-
 183 and-decay pattern in time (Levy et al., 2017). Based on the assumption that at a given time, N₂O fluxes,
 184 F, are typically log-normally distributed in space, the probability density is given by:

$$185 \quad f(F) = 1/(\sqrt{(2\pi)}\sigma_{\log}F)\exp(-((\log(F) - \mu_{\log})^2/(2\sigma_{\log}^2))) \quad (\text{Eq. 2})$$

186 where μ_{\log} and σ_{\log} are the location and scale parameters, equivalent to the mean and standard
 187 deviation of the log-transformed variate.

188 Following a fertilisation event, the time course of N₂O flux is expected to rise to a peak, then
 189 decay exponentially, and this basic pattern is reproduced by all process-based models (i.e. Li et al.,
 190 1992; Del Grosso et al., 2006) and is also well described by the log-normal equation:

$$191 \quad \mu_t = 1/(\sqrt{(2\pi)kt})\exp(-((\log(t) - \Delta)^2/(2k^2))) \cdot N_{in}\Omega \quad (\text{Eq. 3})$$

192 where μ_t is the spatial mean of the N₂O flux at time t, Δ and k are analogues for the location and scale
 193 parameters, and with the additional term N_{in} is the fertiliser nitrogen input and Ω is the fraction of this
 194 which is emitted as N₂O as t tends toward infinity. Δ can be interpreted as the natural logarithm of the
 195 delay between fertiliser application and peak flux; k is a decay rate term. So, at time t following
 196 fertilisation, the mean flux is given by:

$$197 \quad \mu_{\log,t} = \log(\mu_t) - 0.5\sigma_{\log}^2 \quad (\text{Eq. 4})$$

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

$$204 \quad F_{cum,t} = \Phi\left(\frac{\ln t - \Delta}{k}\right) N_{in}\Omega \quad (\text{Eq. 5})$$

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

206 To account for background fluxes (fluxes of N₂O expected in the absence of any applied
 207 nitrogen), a cumulative background flux was estimated using the mean of the fluxes measured from
 208 the control plots during each event. This cumulative background estimate was then subtracted from

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

211 2.4. NH₃ Flux Measurements

212 During the 2016 measurements we were unable to obtain wind tunnels to measure NH₃ flux as originally
 213 planned. Therefore, in 2017 fluxes of NH₃ were derived using the FIDES inverse dispersion model as
 214 described in detail in Loubet et al. (2010 & 2017). This approach requires relatively large plots (20 m²),
 215 and according to the farmers requirements needed to be set up in the Upper Joiner field, diagonally
 216 opposite from the Engineers field. The basis of the model is the solution of the advection-diffusion
 217 equation by (Philip 1959), assuming power law profiles for the wind speed (U(z)) and the vertical
 218 diffusivity (K_z(z)). The model assumes that the atmospheric NH₃ concentration (χ in μg NH₃ m⁻³) at a given
 219 point (x, y, z) is the sum of the background concentration (χ_{bgd} in μg NH₃ m⁻³) unaffected by the sources,
 220 and the influence of the sources (Equation 6). The latter is equal to all the source strengths per unit
 221 surface area (S in μg NH₃ m⁻² s⁻¹) at locations (x_s, y_s, z_s) multiplied by the dispersion function
 222 (D(x_s, y_s, z_s|x, y, z) in s⁻¹), which expresses the contribution of each source to each receptor point at
 223 which the concentration is considered. The meaning of D(x_s, y_s, z_s|x, y, z) can be viewed simply as the
 224 concentration at location (x, y, z) for a source of unit strength at location (x_s, y_s, z_s). (Loubet et al.
 225 2010, 2017)

$$226 \quad \chi_{model}(x, y, z) = \chi_{bgd} + \int_{all\ x_s\ and\ y_s} S(x_s, y_s, z_s) D(x_s, y_s, z_s | x, y, z) \quad (Eq. 6)$$

227 In order to calculate S, D was computed by the model, and both χ and χ_{bgd} were measured. To
 228 calculate D, the description of Philip (1959) was followed as shown in Equation 7 – 10. Here, the values
 229 of a, b, p and n are derived from a linear regression between ln(U), ln(K_z) and ln(z), over the height
 230 range 2 × z₀ to 20 m, using U(z) and K_z(z) estimated based on the Monin-Obukhov similarity theory (e.g.
 231 Kaimal & Finnigan, 1994), where z₀ denotes the roughness length. In Equation 9, X = (x – x_s) sin(WD) –
 232 (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 –
 233 n, ν = (1 – n)/α, and I_{-ν} is the modified Bessel function of the first kind of order –ν. Finally, in Eq. 10 C_y
 234 and m are parameters taken from Sutton (1932).

$$235 \quad U(z) = az^p \quad (Eq. 7)$$

$$236 \quad K_z(z) = bz^n \quad (Eq. 8)$$

$$237 \quad D(X, Y, z) = \frac{1}{\sigma_y \sqrt{2\pi}} \exp\left(-\frac{Y^2}{2\sigma_y^2}\right) \times \frac{zz_s^{(1-n)/2}}{baX} \times \exp\left(-\frac{a(z^\alpha + z_s^\alpha)}{ba^2X}\right) \times I_{-\nu}\left(\frac{2a(zz_s)^\alpha}{ba^2X}\right) \quad (Eq. 9)$$

$$238 \quad \sigma_y = \frac{1}{\sqrt{2}} C_y x^{(2-m)/2} \quad (Eq. 10)$$

239 Wind data were recorded by two sonic anemometers (IRGASON, Campbell Scientific, UT, USA)
240 which were positioned at the north east and south west sides of the plots, 30 m from the borders of
241 the plots in alignment with the two wind predominant wind directions. The anemometers measured
242 3D wind components at 10 Hz. Following Loubet et al. (2001), the source height was tuned to $z_s = 1.01$
243 $z_0 + d$, where d is the displacement height, in order to insure best comparison with Lagrangian Stochastic
244 models and experiments (see also Loubet et al. 2010). The dispersion model embedded in FIDES is
245 essentially similar to the Foken and Meixner (2001) footprint model, except for the retrieval of the a , b ,
246 p , n parameters which are here inferred by fitting the wind speed and diffusivity profiles over a height
247 range 0.2-20 m while in Foken and Meixner (2001) it was computed by forcing the profiles at a reference
248 height. The FIDES model was shown to behave similarly to a Lagrangian Stochastic model in Loubet et
249 al. (2017).

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

266 2.5. Soil Measurements

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

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

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

281 *2.6. Meteorological data*

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

286 **3. Results**

287 *3.1. Crop Yield, NUE and Quality*

288 Although rainfall and temperature was similar during both years of measurement, crop yields for all
289 treatments were substantially larger in the 2016 field plots (5.5 t ha^{-1}) than the 2017 field plots (1.48 t
290 ha^{-1}) (Table 2), indicating that the Engineer's field was the more productive of the two experimental
291 areas regardless of fertiliser application or meteorological conditions. There was reasonably large
292 variation in yield measurements from the harvests in both fields, and in some cases (October 2016) the
293 effect of the addition of fertiliser (i.e. dry control yields subtracted from dry yields of fertilised plots)
294 appeared to have a negative effect on yield (although these values fall well within the large uncertainty
295 range around zero). Overall the most efficient fertiliser overall was ammonium nitrate (Nitram),
296 increasing yields (after subtraction of the control) on average by $1.05 \pm 0.61 \text{ t ha}^{-1}$ with a mean NUE of
297 35.5 %. Urea and inhibitor coated urea increased yields by an average of 0.66 ± 0.62 and $0.69 \pm 0.73 \text{ t}$
298 ha^{-1} , respectively. Nitram treatment was found to increase yields significantly ($p\text{-value} < 0.05$) when
299 compared to the urea fertilisers. The treated urea had a slightly higher average NUE than the untreated
300 urea (24.6 and 20.7 %, respectively), but this difference was not statistically significant ($p\text{-value} = 0.91$).

301 In terms of yield response to the fertilisers, large differences were observed between the two
302 adjacent experimental fields, even though historical management practices were largely similar. In the
303 Engineer's field plots (2016), the response to the fertiliser was muted, with relatively large variation
304 between the plots. Yield response (and standard deviation) of the plots (treated minus control) was
305 largest for the nitram treatments at $19 (\pm 10) \%$, while the urea and inhibitor treated urea had little
306 impact on crop yield, with only a $2.0 (\pm 23) \%$ and $0.7 (\pm 26) \%$ larger harvest when compared to the

307 control plots, respectively. In the Upper Joiner field (2017), the yield response was much higher at 150
308 (± 144), 113 (± 69) and 136 (± 107) % for the nitram, urea and treated urea treatments.

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

317 3.2. N_2O Fluxes

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

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

336 3.3. NH_3 Fluxes

337 Ammonia fluxes were only measured during the 3 fertilisation events in 2017. The majority of the NH_3
338 emissions occurred between 0 and 5 days after fertiliser was applied, and emissions beyond 7 days after
339 fertiliser application were largely negligible. Emissions of NH_3 from the plots varied widely with

340 cumulative flux values from individual plots ranging from -1.8 to 13.1 kg N ha⁻¹ at the end of the 14 day
341 measurement period (Fig. 3 & Table 4). Emissions from the plots treated with urea fertiliser were
342 consistently higher than those of the other treatments after fertiliser applications. Mean cumulative
343 emissions for each of the fertiliser types after all three fertilisation events (n= 12) were -0.74, -0.95,
344 10.83 and 0.42 kg N ha⁻¹ for the control, Nitram, urea and inhibitor treated urea, respectively.

345 Differences in NH₃ from individual plots was typically larger than an order of magnitude of the
346 mean value of the grouped treatments. As the control plots represent a near zero influence situation,
347 the mean flux observed from the control plots for each event were subtracted from the fluxes
348 associated from the treatment measurements. Based on this, emissions from the urea treated plots
349 (mean of 16.5 ± 5.0 % of applied N) were considerably higher than each of the other treatments (-0.3 ±
350 1.8 % and 1.66 ± 2.0 % for Nitram and the inhibitor coated urea, respectively). Fluxes measured from
351 the Nitram plots were not significantly different to those from the control plots (p-value = 0.42), but
352 emissions from the inhibitor coated urea were (p-value < 0.1).

353 3.4. Soil Chemistry

354 As shown in Fig. 4, concentrations of NH₄⁺ varied by several orders of magnitude, with individual
355 measurements ranging from 1.3 to 1525 mg of nitrogen per kg of soil sampled (mg kg⁻¹). Concentrations
356 of NH₄⁺ were consistently low in the experimental plots before fertiliser application; with the exception
357 of the first fertiliser event in 2016 where elevated Nr was observed in the control plots, possibly due to
358 residues from sheep grazing in the field close to one month before the experiment began.
359 Concentrations of NH₄⁺ typically rose in magnitude for several days after fertiliser application before
360 returning to pre-fertiliser magnitudes by the end of the measurement period. Concentrations of NH₄⁺
361 in soils treated with urea and inhibitor coated urea were typically higher than those that received
362 Nitram fertiliser. During the third fertiliser event (13/03/17) there was a clear delay in the rate at which
363 urea was hydrolysed into NH₄⁺ in the soil (Fig. 4). This phenomenon was not observed during the other
364 events.

365 Concentrations of NO₃⁻ followed a log-normal distribution in a similar fashion to the NH₄⁺
366 concentrations (Fig. 5). Nr in the form of NO₃⁻ was typically lower than that of NH₄⁺ with measured
367 values ranging from 0.05 to 165 mg kg⁻¹. As with NH₄⁺, NO₃⁻ concentrations in the experimental plots
368 were near zero before fertiliser application, with the exception of the first event. After Nitram
369 application, NO₃⁻ concentrations typically rose then decreased in concentration with time.

370

371 **4. Discussion**

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

379 The perceived negative effect of fertiliser application during the 2016 trials may have been
380 influenced by a considerably large amount of clover that had begun to grow in the plots by late spring.
381 The nitrogen fixing properties of the clover may have had some impact on the results of the experiment,
382 although not atypical of grazed grasslands (Marriott, 1988). We speculate that the prior grazing of the
383 sheep is also likely to have resulted in the residues of animal waste in the 2016 plots, which would
384 explain the higher than expected yields and Nr in the soil measurements in these plots (Cowan et al.,
385 2015). Although unintentional, the presence of these two factors sheds some light into the importance
386 of N-fixation and animal waste in grazed fields which often receive similar applications of N fertiliser as
387 arable crops. The 2016 plots in our study show that when there is a large amount of Nr already present
388 in the soils, the application of further Nr can have negligible effect on yield response, while still
389 contributing to N pollution. The reason for such high individual concentration measurements of
390 available Nr measured sporadically throughout the experiment are unclear, and may arise as a result of
391 a cluster of fertiliser pellets dissolving in close proximity, or due to outside influences such as urine
392 patches from rabbits or other wild animals. Similar spatial variability in available nitrogen is observed
393 at the field scale in local studies (Cowan et al., 2015; Cowan et al., 2017). The observed ineffectiveness
394 of additional Nr applied to crops in these conditions highlights the future potential of precision farming
395 methods which could take into account the spatial variability of Nr already present in the field and
396 attempt to improve NUE by better managing where fertiliser is required, and where it is not
397 (Auernhammer, 2001; Kindred et al., 2017).

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

406 Emissions of N₂O were higher from the plots treated with Nitram fertiliser than from the other
407 treatments. This observation is consistent with previous research which has identified Nitram as a
408 higher emitter than urea fertiliser (DEFRA, 2006; Harty et al., 2016). Previous studies highlight a
409 potential for pollution swapping with nitrification inhibitor treated urea (typically dicyandiamide, a.k.a.
410 DCD), suggesting that by reducing the rate of conversion of NH₄⁺ to NO₃⁻ in soils that NH₃ emissions are
411 increased (Lam et al., 2016; Zaman et al., 2009). Elevated N₂O and NH₃ emissions have been observed
412 on occasion after the use of nitrification inhibitors (Scheer et al., 2017; Zaman et al., 2009); however
413 reductions in both have also been observed (Di et al., 2006; Misselbrook et al., 2014) . This should not
414 be the case for urease inhibitors as it slows the release of Nr from the applied fertiliser, thus reducing
415 the potential of N₂O and NH₃ emissions. Previous studies have shown that the use of urease inhibitors
416 can significantly reduce N₂O emissions (Singh et al., 2013; Zaman et al., 2009). In this study, emissions
417 from the inhibitor treated urea were slightly larger overall compared to the urea; however, the
418 treatments behaved similarly throughout the experiment and the differences observed in this study
419 were not statistically significant (p-value = 0.42). The emissions of N₂O were not found to correlate well
420 with any of the measured environmental variables such as rainfall or temperature, which is not
421 uncommon. The wide variety of complex interacting conditions that influence microbial processes often
422 prevent predictive modelling and correlation with environmental variables (Butterbach-Bahl et al.,
423 2013).

424 Emissions of NH₃ calculated using the FIDES method were consistently largest from the plots
425 treated with urea fertiliser (mean EF of 16.5 % of applied Nr). The emissions from the Nitram plots were
426 not significantly different from the control plots, suggesting that emissions were negligible from this
427 treatment. These observations agree with previous studies in that urea treatments are expected to lose
428 a large fraction of Nr as NH₃ emissions (Sommer et al., 2004) while Nitram treatments do not (DEFRA,
429 2005). The urease inhibitor appears to have significantly reduced NH₃ losses from the inhibitor coated
430 urea plots, reducing emissions of NH₃ by approximately 90 % when compared to the untreated urea.
431 This effect has been observed in other similar studies when applying a urease inhibitor to urea fertiliser
432 (Li et al., 2015; Rawluk et al., 2001). The large reduction in NH₃ volatilisation and lack of yield response
433 does raise the question of the fate of the Nr in the urease treated urea plots.

434 After the N content of the crop, the N content of the soil and emissions of N₂O and NH₃ are
435 taken into account, the majority (> 55 %) of applied Nr in the experiments remains unaccounted for by
436 the time of harvest. Typically, Nr in the form of NH₄⁺ and NO₃⁻ in the top 10 cm of soil has returned to
437 concentrations on par with the control plots by harvest. When compared to the control plots, the
438 remaining extractable Nr in the top 10 cm of the fertiliser treated plots at time of harvest accounted
439 for less than 1 % of the applied nitrogen in all cases in this study. Other known pathways for large losses
440 of Nr from agricultural soils include the leaching of NO₃⁻ into deeper soils and water systems, uptake of
441 Nr into root systems, and microbial nitrification and denitrification which produces nitric oxide (NO)

442 and gaseous nitrogen (N₂). Leaching can account for 2 - 33 % of applied Nr (Riley et al. 2001; Sebiló et
443 al. 2013; Skinner et al. 1997), root systems may consume Nr in the same order of magnitude as the
444 harvested shoots (Watson, 1987) and microbial emissions of NO and N₂ can account for Nr losses of an
445 order of magnitude higher than N₂O when water filled pore space (WFPS) is particularly low (< 40 %) or
446 high (> 80 %) (Davidson 1993; Weier 1993). All of these potential processes may account for a significant
447 fraction of the unaccounted Nr applied to the plots in this experiment and measurements should be
448 included in future studies when logistically possible.

449 **5. Conclusions**

450 Large variations in crop yield measurements show that none of the fertiliser types used in this study
451 consistently outperforms the others in terms of NUE. However, of the three fertilisers used, Nitram
452 performed better on average than the urea compounds in this experiment with an average NUE of 35%
453 when compared to urea (21 %) and the inhibitor treated urea (24 %). This study supports previous
454 research which suggests that Nitram is the largest emitter of N₂O (0.76 % of applied Nr) and that urea
455 fertiliser is the largest emitter of NH₃ (16.5 % of applied Nr) when the mineral fertilisers are compared.
456 The use of the urease inhibitor resulted in a considerably large reduction in NH₃ losses from the urea
457 fertiliser (decrease of 90 %) without significantly increasing emissions of N₂O; however, yields were
458 statistically the same. The results of this study suggest that urease inhibitors, such as Agrotain®, can
459 play an important role in mitigating Nr-related air pollution. However the agronomic benefits to the
460 farmer appear to be negligible. With the higher costs of urea coated with urease inhibitors, there is no
461 incentive for farmers to switch to these more environmentally friendly compounds. Our experiments
462 are short term only. There certainly is a need for more long-term studies covering different climate
463 zones, crop types and soil properties to investigate the economic and environmental benefits of
464 switching from the preferred ammonium nitrate fertilisers in the UK to urea treated with urease
465 inhibitors, or even double inhibition using nitrification and urease inhibitors.

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474 **7. Author Contribution**

475 N. Cowan managed the fieldwork, carried out data analysis and wrote the manuscript. P. Levy
476 contributed to the Bayesian statistics and was involved in the writing of the manuscript. A. Moring, B.
477 Loubet and P. Voylokov worked on the data analysis and the FIDES method. I. Simmons, C. Bache, A.
478 Stephens, J. Marinheiro, J. Brichet, L. Song, A. Pickard, C. McNeill, R. McDonald and J. Maire were
479 involved in the fieldwork and laboratory analysis stages of the research. M. Sutton provided guidance
480 on the measurement aspects of ammonia and helped develop the data analysis. U. Skiba is the primary
481 investigator of the Cinag project at CEH Edinburgh, managing the project overall, contributing to all
482 aspects of the research and the writing of the manuscript.

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669 **Table 1** Management of experimental plots over five fertilization events at Easter Bush Farm, 2016 &
670 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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673 **Table 2** Crop quality measurements of sub-samples taken from harvests of all experimental treatment
 674 plots. Mean values and standard deviation of samples are provided (n = 4 replicates). Effect of N
 675 addition is reported as the additional dry matter (DM) harvested compared to the control plots. The
 676 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 (%)
<u>2016</u>						
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
<u>2017</u>						
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

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679 **Table 3** Cumulative N₂O fluxes estimated using the Bayesian interpolation method over a 30 day period
 680 after fertilizer applications (70 kg N ha⁻¹) at two intensively managed grassland sites. Values presented
 681 represent 4 plots (n = 4) per event at each field site. Emission factors (EF) account for the effect of N
 682 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.		Flux Minus Background (kg N ha ⁻¹)	EF (%)
				min	max		
<u>2016</u>							
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
<u>2017</u>							
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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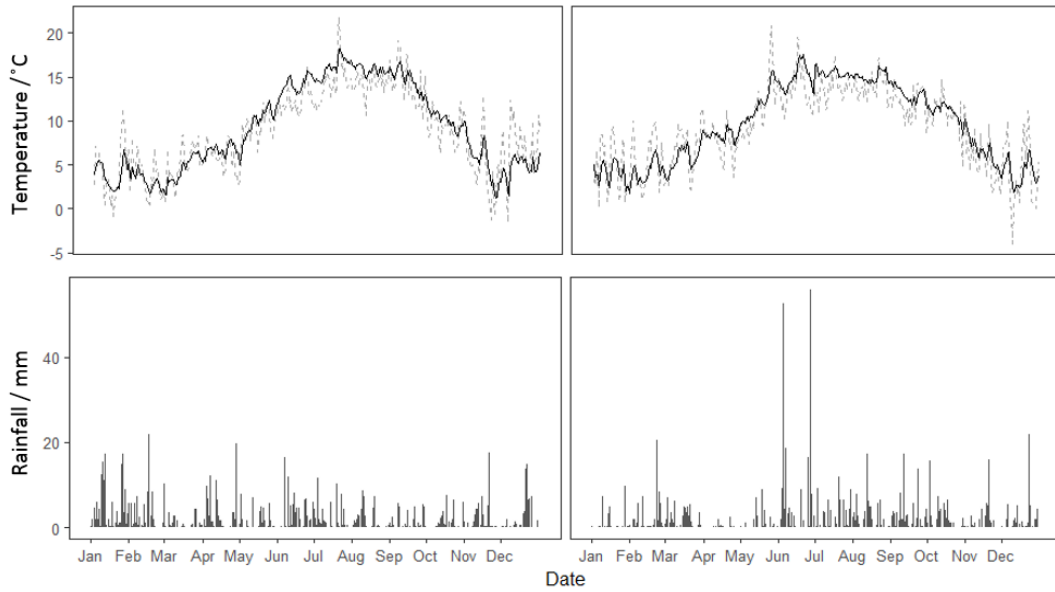
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685 **Table 4** Cumulative fluxes of NH₃ estimated the FIDES method over a 14 day period after fertilizer
 686 applications (70 kg N ha⁻¹) at the Upper Joiner grassland. Values presented represent 4 plots (n = 4) per
 687 event at each field site. Emission factors account for the effect of N application after the measured
 688 background flux has been deducted from cumulative totals. The 95 % C.I. is calculated using the least
 689 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

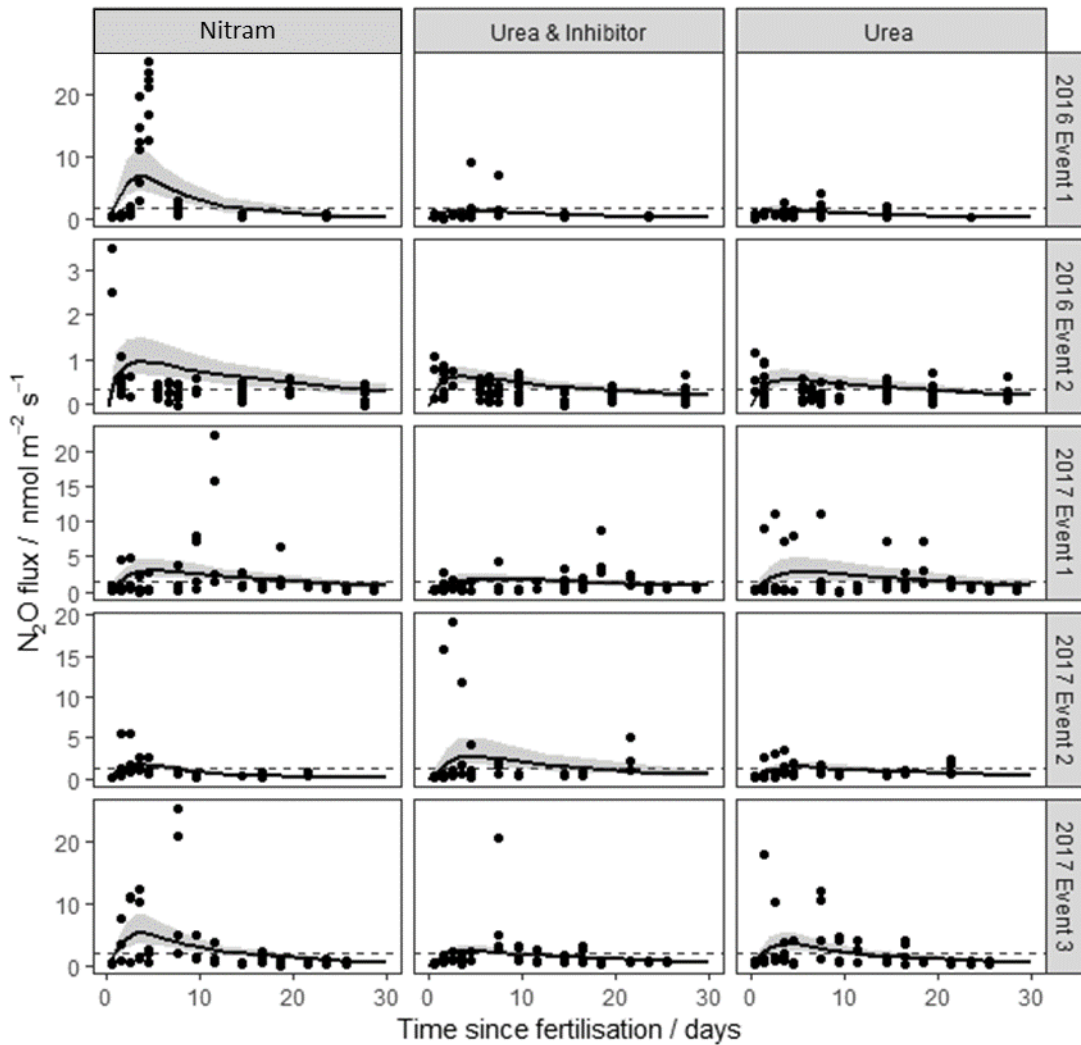
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Figure 1 Meteorological data recorded at Easter Bush Farm over 2016 (left) and 2017 (right). Daily mean soil temperature (black) and air temperature (grey) and daily cumulative rainfall are presented.



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Figure 2 N₂O fluxes following fertilisation of the Engineer's field in 2016 and Upper Joiner field in 2017.

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Fertiliser was applied at t = 0 days, and the measurements lasted up to 30 days for each event. The log-

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normal model was used to estimate cumulative N₂O fluxes. The 95 % credible intervals of the posterior

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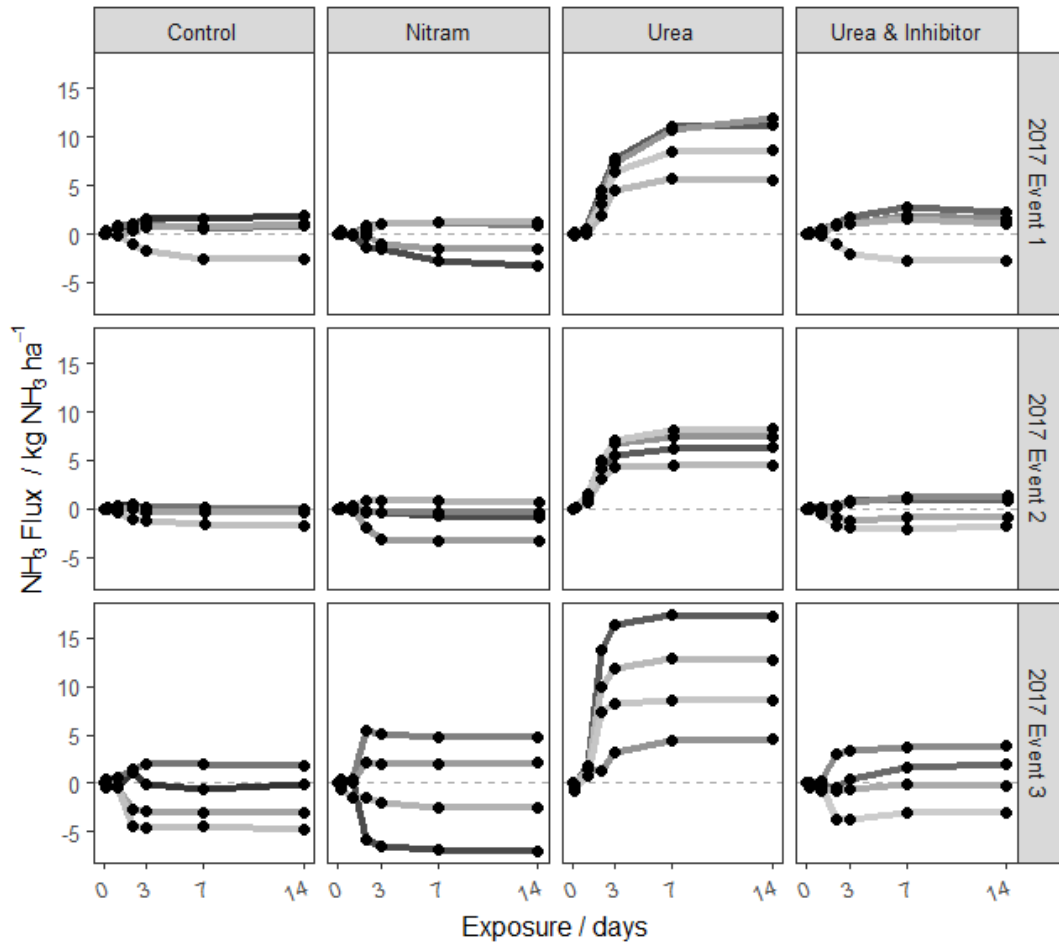
predictions are shown as the shaded area. Mean background fluxes from control plots are included for

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each event (dashed line).

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Figure 3 Cumulative fluxes from each of the experimental plots during three fertilisation events

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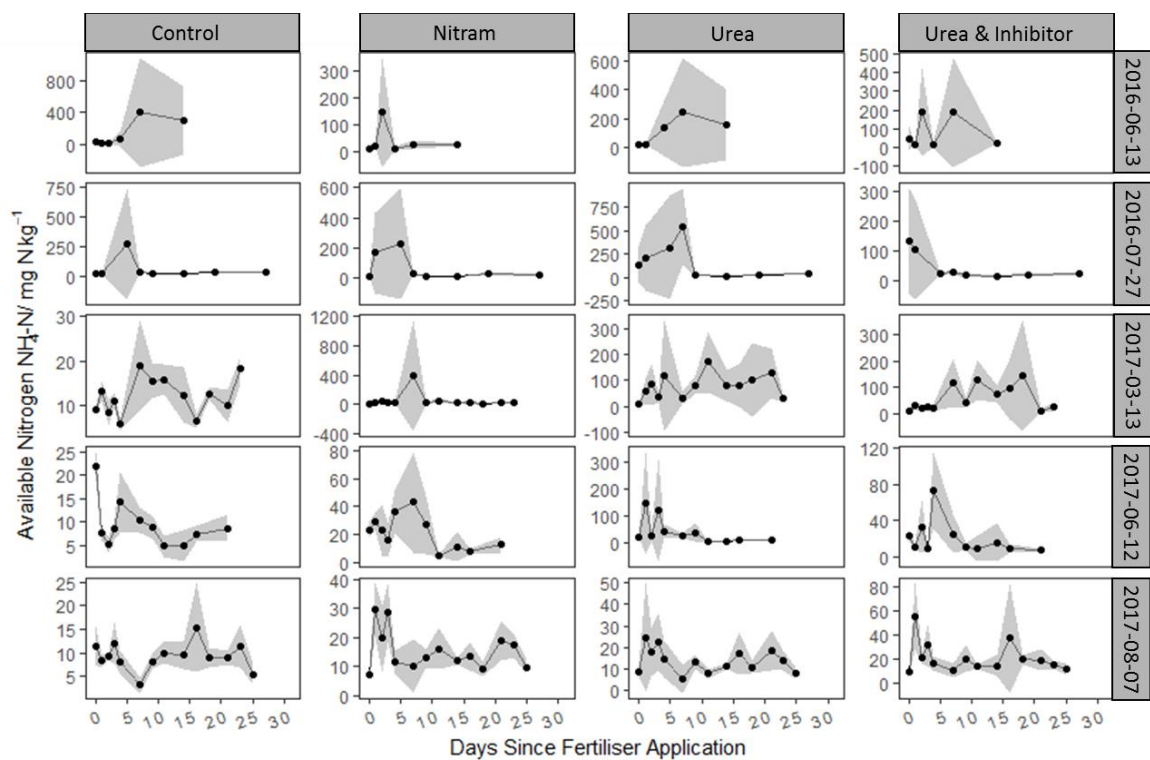
measured using the FIDES method (2017). Each shaded line represents one of the four plots replicated

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for each treatment.

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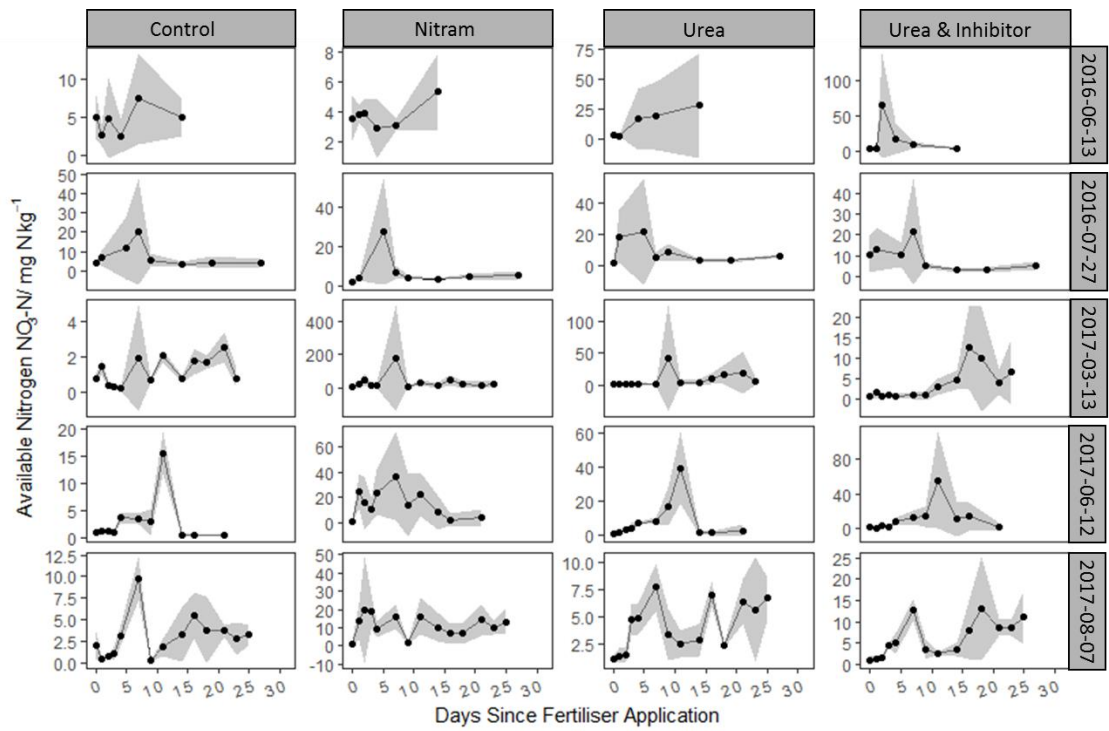


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712 **Figure 4** Mean ammonium concentrations from soil samples (n= 4) measured in tandem with N₂O

713 chamber measurements after fertilisation events. Standard deviation is included (grey ribbon).

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Figure 5 Mean nitrate concentrations from soil samples (n= 4) measured in tandem with N₂O chamber

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measurements after fertilisation events. Standard deviation is included (grey ribbon).