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Assessing the benefits and wider costs of different N fertilisers for grassland agriculture

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Abstract

Fertiliser nitrogen (N) is essential for maintaining agronomic outputs for our growing population. However, the societal, economic and environmental impacts of excess reactive N from fertiliser is rarely assessed. Here the agronomic, economic and environmental efficacy of three N-fertiliser sources, ammonium-nitrate (AN), urea (U), and inhibited-urea (IU; with NPBT) were evaluated at two grassland sites. Dry matter yield and herbage quality was measured at each silage-cut. Additionally, NH_3-N and N_2O-N losses were measured and used to calculate the effective N source cost and externality costs, which account for associated environmental and societal impacts. We found no effect of different N sources on yield or herbage quality. However, NH_3-N emissions were significantly reduced under the IU treatment, by 48-65%. No significant differences in cumulative N_2O emissions were observed. Incorporating externality costs increased fertiliser prices by 1.23-2.36, 6.51-16.4, and 3.17-4.17 times the original cost, for AN, U and IU, respectively, transforming U from the cheapest, to the most expensive of the N sources examined. However, with no apparent yield differences between N-fertiliser sources there is no economic incentive for the land-manager to use the more environmentally and socially acceptable option, unless externality costs are incorporated into fertiliser prices at the point of sale.

Keywords: ammonia; fertilizer management; greenhouse gas emissions; urease inhibitor; nitrous oxide.

Introduction

Nitrogen (N) fertilisers are essential for feeding and maintaining our rapidly growing global population. However, through the production and use of synthesised N fertiliser, the global N cycle has become massively disrupted (Rockström et al. 2009). Globally the production of N fertiliser reached 104–113 M tonnes N year^{-1} (years 2010 – 2014; FAO~~STAT~~ 2016). Nitrogen fertilisers are particularly reactive and, where they are not efficiently used by the target crop, can quickly be transported out of the agricultural system. A recent estimate of full chain N use efficiency (NUE) across 24 EU countries, where NUE was calculated based on N input as fertiliser and N outputs in the final foodstuff, was just over 30% (Erisman et al. 2015). Alternative N fertilisers have been developed with the aim of reducing N losses. These fertilisers include N cycling inhibitors such as urea (U) in combination with the urease inhibitor N-(*n*-butyl) thiophosphoric triamide (NBPT). Such fertiliser formulations are marketed as reducing N losses, thereby increasing the N available for crop uptake, leading to yield improvements. Multiple studies have been conducted to examine the role of inhibited N-fertilisers on soil mineral N (grassland, Zaman et al. 2013; fallow systems, Degenhardt et al. 2016), nitrous oxide (N_2O) emissions (grassland, Dobbie and Smith 2003; spring barley, Roche et al. 2016; laboratory study, Awale and Chatterjee 2017), ammonia (NH_3) emissions (grassland, Suter et al. 2013; grassland, Forrestal et al. 2016; laboratory study, Awale and

Chatterjee 2017), and yield (grassland, Suter et al. 2013; grassland, Zaman et al. 2013; meta-analysis, Abalos et al. 2014; spring barley, Roche et al. 2016; grassland, Harty et al. 2017). However, they typically focus on specific aspects of N cycling such as denitrification or NH_3 volatilisation. To enable comparison of novel N fertilisers with conventional N fertilisers a whole system approach considering multiple N-loss pathways, crop yield and quality, and economics is required.

Within the UK, U is increasingly being used as an alternative N fertiliser to ammonium-nitrate (AN; British Survey of Fertiliser Practice 2016). Of these two N fertilisers, U has a greater N content than AN at 46% relative to 35% respectively, and the price per kg of N is typically less than that of AN. However, U can be susceptible to large NH_3 losses, which can range 5 – 68% of the fertiliser-N applied (Ryden et al. 1987; Chambers and Dampney 2009; Schwenke et al. 2014; Forrestal et al. 2016), compared with < 3% (Ryden et al. 1987; < 2%, van der Weerden and Jarvis 1997) for AN. However, AN may be susceptible to greater N losses as N_2O via denitrification, particularly when application is followed by rainfall (Ryden 1983; Sexstone et al. 1985; Chambers and Dampney 2009; Smith et al. 2012). These N losses from N fertiliser represent a direct economic cost to the land manager and may result in yield reductions. As such, land managers may be faced with a trade-off between fertiliser-N cost, agronomic and environmental performance. Associated N-losses may also have large externality costs to society in general through environmental damage, human health impacts and global warming (Sutton et al. 2011). However, these costs are not included in the fertiliser price and are unlikely to influence fertiliser choice.

Urea-based products containing urease inhibitors, such as NBPT, may provide a viable alternative to U and AN, but more information is needed to determine the relative agronomic, environmental and economic performance of U, AN and urease inhibited urea (IU). We examined the performance of AN, U and IU (NBPT as the urease inhibitor; Agrotain®; from Koch Agronomic Service), along with a control (C; without N addition) at two intensive grassland sites, both managed as three-cut silage systems. Measured parameters for our N budget included the N-loss pathways of NH_3 volatilisation and N_2O emissions, herbage-N content and dry matter yield. Our aim was to determine how the three different N sources performed in terms of N-losses to the environment, crop offtake and quality. We also assessed the wider impact of the fertiliser N-losses through calculation of externality costs. We hypothesised:

1. DM yields and grass quality under U would be less than that of AN and IU, due to increased N-losses via NH_3 emissions
2. IU would reduce NH_3 emissions relative to U, resulting in
3. Greater N availability under IU relative to U for crop N-offtake and for N-losses as N_2O
4. Calculated externality costs would be greatest for U

Materials and methods

Field sites and soil characteristics

Two plot trials were conducted during the 2016 growing season at grassland sites in the UK. The first site was at Henfaes Research Station, Abergwyngregyn, Wales (53°14′N, 4°01′W; 10 m a.s.l.), hereafter referred to as HF. The HF site has a temperate, oceanic climate, with average annual rainfall of 1250 mm and mean annual soil temperature at 10 cm depth of 11°C (Shaw et al. 2016). The HF ley was established in 2014 with a *Lolium multiflorum* (Italian ryegrass), and *Trifolium pratense* (red clover) and *Trifolium repens* (white clover) mixture (75 and 25% respectively). Prior to this study, the HF site was managed for summer silage production and winter grazing. All livestock were removed in March 2016 and lime additions of 2.6 t ha^{-1} were made to achieve a soil pH of 6.5. The HF soil is a free-draining Eutric Cambisol with a sandy clay loam texture and a fine crumb structure. The second site was at Rothamsted Research, North Wyke, southwest England (50°46′N, 3°55′W; approximately 182 m a.s.l.), hereafter referred to as NW. The NW site has a temperate climate with average annual rainfall of 1107 mm and mean annual soil temperature at 10 cm depth of 12°C (Rennie et al. 2017). The NW ley was established in 2015 with a *Lolium perenne* (perennial ryegrass), white clover, and herb mixture (92.5%, 5%, and 2.5% respectively). The NW soil is a seasonally-waterlogged Endoleptic Stagnic Cambisol with a silty clay loam texture. The background soil characteristics of both sites are presented in Table 1.

Experimental design and plot layout

At both sites, the grassland was managed as a three-cut silage system, with a total N application of 240 kg N ha^{-1} (recommended for sites with a good grass growth class; Defra 2010). Fertiliser-N treatments were AN, U and IU, as well as the C. All plots received P, K, and S in accordance with national fertiliser guidelines (Defra 2010). Each treatment was replicated four times ($n = 4$) making a total of sixteen plots at each site, arranged in a randomised complete-block design. Plots were further divided into three sub-plots. Sub-plot one (4 x 2 m) was designated for NH_3 emission measurements, sub-plot two (2 x 2 m) was designated for soil sampling and N_2O emission measurements, and sub-plot three (6 x 2 m) was designated for harvesting and yield determinations. Fertiliser was applied by hand to the plots and was applied separately within the N_2O chamber bases. All fertiliser additions and timings are summarised in the online-supplementary information (Table S.1).

Quantifying herbage production and quality

At the HF site a 1.27 m strip was cut down the centre of each harvest sub-plot to a residual height of 5 cm. The cut herbage was collected and total fresh weight measured. Representative sub-samples (~ 200 g) were collected, and then dried at 80°C for 72 h to determine dry matter yields. Dried herbage samples were analysed for herbage quality, including crude protein (CP), metabolisable energy (*ME*), and dry matter (DM) (Sciantec Analytical Laboratories, Stockbridge Technology Centre, York, UK). Digestibility (*D*, %) was determined following equation 1.

$$D = ME / 0.16$$ (~~equation~~ 1)

For each silage cut at NW, a 1.5 m strip was cut down the centre of each harvest sub-plot to a residual height of 5 cm and the fresh herbage weighed immediately using a Haldrup small plot harvester. Representative samples (~ 2 kg) were taken manually and analysed for the same herbage quality analyses as described for HF (Trouw Nutrition GB, Blenheim House, Ashbourne, UK).

Ammonia emissions

Ammonia volatilisation was measured using a system of small wind tunnels (Misselbrook et al. 2005). Wind tunnels were run continuously for three weeks following each fertiliser split-application, with 0.02 M H_3PO_4 acid traps (100 ml) changed at a daily resolution. Wind tunnels were moved daily to one of three positions, with a return to position one on the fourth day. This was carried out to minimise the impact of the tunnel canopy on the plot area.

Ammonia fluxes from the measurement area (F_{NH3}, μg m^{-2} s^{-1}) were determined for each measurement period using equation 2:

$$F_{NH3} = (C_o - C_i)\, v/t$$

(~~equation~~ 2)

where C_o and C_i were the NH_3-N concentrations (μg NH_3-N m^{-3}) at the tunnel inlet and outlet , respectively, and v was the air volume (m^3) drawn through the wind tunnel over the sampling period (t, s).

At NW, NH_3 emissions were measured from the AN, IU and U treatments ($n = 4$), whereas at HF, measurements were conducted from the U and IU treatments only ($n = 3$ for the first N application, $n = 4$ for the second and third N applications). The acid trap samples were taken from the field, topped up to 100 ml with deionised H_2O and a subsample taken and stored at 4°C (NW) or -18°C (HF) prior to colorimetric analysis ~~(Mulvaney 1996~~). Cumulative NH_3 emissions were calculated for each plot for the three N-application periods using the area under a curve function “cumtrapz()” from the “pracma” package (~~Hans Werner~~ Borchers, 2016) in R (version 3.3.2; R Core Team~~,~~ 2016). More information on the cumulative NH_3

Commented [d1]: Missing in reference list emission calculations and data censoring can be found in the online-supplementary information (S.2.).

Nitrous oxide emissions

Nitrous oxide emissions were measured on each plot (*n* = 4), using static manual chambers at NW and a combination of static manual and static automatic chambers (combined with an Isotopic N_2O Analyser, Los Gatos Research Inc. San Jose, CA, USA) at HF. Following the first N application at HF, fluxes from the C treatment were measured using static manual chambers, whereas static automatic chambers were used for all other treatments (*n* = 4 for each treatment). For the second and third N-applications at HF, only static automatic chambers were used across all treatments. Measurement replication was thus reduced to three of the four experimental blocks (*n* = 3 for each treatment).

Where manual chambers were used, slots were cut into the soil and the chambers (50 × 50 × 30 cm) inserted, so they projected 15 – 20 cm above the soil surface. Soil was packed around the outside of the chamber to ensure a good seal. Chambers were installed two weeks prior to the start of the experiment, removed prior to herbage cutting events and replaced immediately after. Following ~~fertilizer~~ fertiliser application, N_2O sampling from the manual chambers was performed three times weekly for the first and second weeks, twice weekly for the third and fourth weeks, and once weekly thereafter. Sampling was carried out between 10:00 and 12:00 am (according to Cardenas et al. 2010), using the protocol of de Klein and Harvey (2012). On each sampling occasion, lids were placed on the chambers and remained in place for 40 min with headspace samples taken at 0, 20 and 40 min from each chamber. Gas samples were analysed for N_2O concentration using a Perkin Elmer 580 Gas Chromatograph (linked to a TurboMatrix 110 headspace autosampler).

At HF, the automatic chambers were installed two weeks prior to the start of the experiment, the chamber bases were inserted into the soil and the chambers (50 × 50 × 20 cm) attached to the bases at surface height to ensure an air tight seal. Closing and opening of the chambers was controlled by pneumatic actuators. The chambers closed sequentially for a 30 min period, during which the chamber-headspace was sampled via a sampling port at a rate of 1 l min^{-1}. Samples were delivered to an Isotopic N_2O Analyser and N_2O concentrations recorded at 0.1 Hz for each 30 min sampling period. The first 30 s of data from each sampling period was removed from calculations to account for the dead volume in the sample lines. Accuracy of the N_2O analysis was checked weekly using certified N_2O standards.

Hourly N_2O fluxes (µg N_2O-N m^{-2} h^{-1}) were calculated using linear regression, with the assumption of linearity. Calculations on the automatic chamber data set were made using the lm() function in R (version 3.3.2., R Core Team 2016). The manual chamber data set were calculated according to de Klein and Harvey (2012; Excel, Office 2016) using equation 3:

$$F_{N2O} = H(C_t - Ct_0)/t \qquad \text{(~~equation~~ 3)}$$

where H is the ratio of chamber volume to soil surface area (m^3 to m^{-2}), C_t is the concentration of N_2O within the chamber at the time (t) of sampling and C_{t0} is the N_2O concentration measured at 0 min, measured after the chamber had been sealed. More details on the calculations and data censoring can be found in the on-line supplementary information (S.3.).

Cumulative N_2O emissions were calculated for each plot for the three N-application periods using the area under a curve function "cumtrapz()" from the "pracma" package (~~Hans Werner~~ Borchers 2016) in R (R Core Team 2016).

Farm and externality costs

To calculate on-farm and environmental externality costs a basic N-budget was created for each N treatment. Fertiliser N input costs were calculated using December 2015 UK prices of € 0.90, € 0.69 and € 0.82 kg N^{-1} (cost at time of purchase; PoundSterling LIVE 2017) for AN, U and IU respectively. Gaseous N losses for each treatment were based on the summation of the mean NH_3 and N_2O cumulative emissions from each N application (with C emissions subtracted). As there were no measurements of NH_3 emissions from the AN treatment at Henfaes, an emission rate of 1.3% was assumed for these calculations (European

Environment Agency 2016). These N-losses were then converted to an economic loss based on the fertiliser prices given above. No attempt was made to quantify N leaching, as it was assumed to be minimal during the growing season. Furthermore, at both sites, soil NO_3^- for all N treatments was comparable to that of C at the end of the experimental period (see supplementary information S.5), which suggests little residual fertiliser-N was available for leaching. The gaseous losses enable calculation of the effective fertiliser input (*EFI*) – i.e. that which would be available for plant uptake:

$$EFI = FI - gaseous\ N\ losses$$ (~~equation~~ 4)

where *EFI* is the effective fertiliser input (kg N ha^{-1}), *FI* is the actual fertiliser input (kg N ha^{-1}) and *gaseous N losses* is the sum of N-losses via NH_3 and N_2O emissions. This ignores N_2 and NO losses, which were not measured in this study, and N_2 losses were likely to be significant.

In turn, this allows a recalculation of the unit cost of the fertiliser to account for these losses, the effective fertiliser cost (*EFC*):

$$EFC = (FC \times N_{rate})/EFI$$ (~~equation~~ 5)

where *EFC* is the effective fertiliser cost (€/kg N), *FC* is the actual fertiliser cost (€/kg N), N_{rate} is rate at which the fertiliser was applied (kg N ha^{-1}) and *EFI* is the effective fertiliser input (kg N ha^{-1}).

It is well documented that these gaseous N losses have a negative effect on the environment and human health (Sutton et al. 2011). Based on the polluter pays principle, including these externality costs into the fertiliser costs may have a large effect on the economic N optimum and N fertiliser choice. Externality costs of € 14 kg NH_3-N^{-1} and € 11 kg N_2O-N^{-1} respectively, (based on figures from Brink and van Grinsven 2011), were attributed to the gaseous N losses. These costs were then used to adjust the *EFC* accordingly:

$$EFC_{env} = ((FC \times N_{rate})+C_{env})/\ EFI).$$ (~~equation~~ 6)

where EFC_{env} is the effective fertiliser cost adjusted for environmental externalities (€/kg N), FC is the actual fertiliser cost (€/kg N), N_{rate} is rate at which the fertiliser was applied (kg N ha^{-1}), C_{env} is the associated externality cost arising from gaseous N emissions, and EFI is the effective fertiliser input (kg N ha^{-1}).

Herbage N offtake

N content in the grass was calculated from the crude protein results using a factor of 6.25. Herbage N offtake (*N-off*) was then calculated as follows:

$$N\text{-}off = N_{content} \times yield$$

(~~equation~~ 7)

where $N_{content}$ of the grass as a percentage and *yield* is the grass offtake from each plot (kg dry matter ha^{-1})

Statistical analysis

Overall differences, and within N application differences, at both sites were assessed using Analysis of Variance (ANOVA) with a blocking factor, followed by Tukeys post-hoc test. Within sites, the randomised complete block experimental design was defined as the blocking factor within ANOVA, whereas site was defined as the blocking factor when ANOVA was used for data from both sites. Parameters assessed were herbage yield, herbage quality and gaseous emissions between treatments. Both tests were performed using functions aov() and TukeyHSD() in R (R Core Team 2016). Where appropriate, the dependent variable was log transformed to ensure the assumptions of ANOVA were met. Statistical significance is defined as $p < 0.05$.

Results

Herbage production

At both sites, all N fertilisers produced a significantly greater herbage yield than C, at N applications 1 and 2 at NW, and N application 2 at HF. Overall the U treatment resulted in the highest total yields (Fig~~.~~ure 1), although this was not significantly greater than that of the other N treatments. At both sites, there were significant differences in herbage yield between the three N-application periods. At HF, the herbage yield from the first N-application was significantly greater than that from the second or third N-application (~~Fig.~~Figure 1). At NW, there were significant differences in the herbage yields between the three N applications with the greatest yields achieved following the second N-application. There was also a significant interaction between fertiliser treatment and harvest, which can be attributed to the performance of C (~~Fig.~~Figure 1).

Herbage quality and NUE

In general, herbage from NW had a higher *CP* content, *D* value and *ME* than at HF (mean values; ~~Fig.~~Figure 2). At both sites for all three quality indicators (*CP*, *D* and *ME*), there were no overall significant differences between any of the N treatments. At both sites overall, *CP* from the C treatment was significantly greater than all the N treatments, and this was mainly apparent in the second and third applications. The greatest herbage *CP* content was observed for C following N application three at NW, at 241.0 ± 17.0 g *CP* kg^{-1}. At all harvests at NW the C treatment generally had greater *D* values and *ME* than that of all the N treatments. At HF, the *D* value and *ME* for IU was significantly greater than for U following N application one, for N applications two and three there were no significant differences for *D* value and *ME* between any of the treatments.

Within both sites, there were no significant differences in N offtake between any of the treatments (Table 2), with mean values of 370, 363 and 387 kg N ha^{-1} and 312, 338 and 313 kg N ha^{-1} for AN, U and IU, at HF and NW respectively. Although it was numerically lower at both sites for C at 342 and 298 kg N ha^{-1} for HF and NW respectively. Greatest N offtake was from the IU treatment at HF and U at NW. N offtakes were higher at HF than at NW for all treatments.

NH_3 emissions

At HF, NH_3 emissions were only measured from the U and IU treatments and were significantly greatest from U. Cumulative NH_3 emissions were significantly greatest following the second N application, where emissions were 65.6 ±10.2 and 24.9 ± 6.5 kg N ha^{-1} from U and IU respectively (~~Fig.~~Figure 3). Following the first and third N application, NH_3 emissions were 20.5 ± 7.0 and 14.1 ± 3.6 kg N ha^{-1} for U and 5.5 ± 2.8 and 4.9 ± 1.7 kg N ha^{-1} for IU. The use of IU compared to U reduced NH_3 emissions by 73, 62 and 65%, respectively, for the three N applications. Total cumulative emissions (Table 2, calculated by summing the means from the three N applications) represented 42% and 15% of the total applied fertiliser N for U and IU respectively. At NW, cumulative NH_3 emissions from U were significantly greater than both IU and AN. Cumulative emissions for U and IU were generally lower than those observed at HF, with the greatest emissions of 22.5 ± 2.4 kg N ha^{-1} from U following the third N application. Following all N applications, NH_3 emissions were greatest from U, with IU reducing emissions by 54, 57 and 40% following the first, second and third N applications respectively. Additionally, emissions from AN did not exceed 6.8 ± 1.0 kg N ha^{-1} and were not significantly different from IU. Total cumulative NH_3 emissions represented 7, 21 and 11% of the total applied N for AN, U and IU respectively.

N_2O emissions

At HF, there were significant differences in cumulative N_2O emissions between U and C, IU and C, and IU and C for N applications one, two and three respectively. However, there were no significant differences between any of the N treatments for any given application (~~Fig.~~Figure 4, see also Figure S.1. in supplementary information for the N_2O time series). Cumulative emissions were lowest following the first application and did not exceed 0.06 ± 0.00 kg N_2O-N ha^{-1}. Cumulative N_2O emissions were greater following the second and third N applications, in the order IU > U > AN > C, with 0.43 ± 0.12 kg N_2O-N ha^{-1} from IU following the third application.

At NW, cumulative emissions (~~Fig.~~Figure 4, see supplementary information Figure S.2. for N_2O time series dataset) from the first and second N applications were significantly greater than those of the third, but not significantly different from each other. Cumulative emissions following the third N application were very low and did not exceed 0.11 ± 0.04 kg N_2O-N ha^{-1} from any of the treatments. The greatest cumulative emissions, of 1.29 ± 0.24 kg N_2O-N ha^{-1}, were from AN following the first application, which was significantly greater than all other treatments within this application.

N budget, farm and externality costs

Of the three N fertilisers, U was the cheapest per unit of N to purchase at 0.69 € kg N^{-1}, and AN the most expensive at 0.90 € kg N^{-1} (Table 2). However, at both sites, total gaseous N losses were highest from U, with losses of 101 and 49 kg N ha^{-1} from HF and NW, respectively, corresponding to a direct economic loss for the farmer of € 69 and € 34 ha^{-1} respectively. At both sites, AN had the lowest total N emissions, with 3 and 18 kg N ha^{-1}, corresponding to an economic loss of € 3 and € 17 for HF and NW respectively (Table 2). Gaseous emissions of N from U were 1.9 - 2.8 times greater than from IU. Comparisons based on the effective fertiliser cost, which account for the direct economic costs associated with the gaseous N losses, showed that AN was the most cost effective fertiliser at HF at 0.91 € kg N^{-1} (Table 2). However, this was only marginally less than IU, and U was the least cost effective at 1.19 € kg N^{-1}. At NW, IU was the most cost effective at 0.82 € kg N^{-1} and AN was the least cost effective at 0.97 € kg N^{-1} (Table 2).

Adding externality costs to the effective fertiliser costs greatly increased the unit cost of all three of the N fertilisers (Table 2). At both sites, U became the most expensive fertiliser due to large NH_3 emissions, with effective externality fertiliser cost of 11.30 and 4.49 € kg N^{-1} at HF and NW respectively, whilst AN became the cheapest at 1.11 and 2.12 € kg N^{-1} at HF and NW respectively.

Discussion

Herbage production and quality

In this study, no significant differences in herbage yield were found between the three N fertilisers, although all three N fertilisers produced significantly higher yields than the C. This result is contrary to the meta-analysis of Abalos et al. (2014), which showed an average increase of 10% in crop productivity under IU when compared to U. Similarly, in another pasture-based study, Zaman et al. (2013) observed greater DM yields with IU, at both low and high N rates (150-180, and 300-350 kg N ha^{-1}) compared to U. However, as in our study, Harty et al. (2017) found no effect of the N sources, U, IU and calcium AN on perennial ryegrass (*Lolium perenne* L.) DM yield. In addition, Suter et al. (2013) reported a 21% reduction in NH_3 emissions with IU relative to U, but did not observe a yield gain, which the authors attribute to soil N supply being non-limiting. These mixed results, in addition with those from this study, suggest that additional factors, such as soil N supply (see supplementary online information S.5 and Figure S.3.), can exert a greater influence on DM yield than can be observed with the IU treatment relative to U.

Another factor that may have affected plant N availability in this study was the presence of clover within the sward. White clover is acknowledged to be a particularly efficient N donor to neighbouring plants (Pirhofer-Walzl et al. 2012). Consequently, biological N fixation, and subsequent rhizodeposition of N, provided an additional N source to the growing sward (Fustec et al. 2010). This additional N source is likely to have been greatest under the C treatment, where lower N inputs can lead to greater clover content, consequently increasing biological N fixation and thus N supply (Reid 1970; Høgh-Jensen and Schjoerring, 1997). This proliferation of clover may explain the relatively high N offtake, and CP content observed under the C treatment (~~Fig.~~Figure 2, Table 2), particularly following the second and third N application when clover is more prevalent within the sward. In terms of herbage quality, there were no differences between the N treatments in any of the metrics evaluated.

Due to these findings, we reject our first hypothesis that DM yields and herbage quality would be lower from U, compared to IU and AN, despite increased losses of N from U via NH_3 emissions.

NH_3 emissions

NH_3 emissions under U were consistently the greatest of the three N treatments, at both sites. However cumulative NH_3 emissions under U varied greatly between sites (~~Fig.~~Figure 3 and Table 2), with 21 and 42% of the N applied lost as NH_3 at NW and HF respectively. Significant differences in NH_3 losses between sites were also observed by Forrestal et al. (2016), with losses of 20 – 53% and 8 – 33% at the Johnston Castle and Hillsborough sites respectively, under U fertiliser at 200 kg N ha^{-1}. Differences between sites are somewhat unsurprising as NH_3 emissions are strongly related to: (1) precipitation, if great enough (e.g. > 14.6 mm d^{-1}; Holcomb et al. 2011) can solubilise and transport urea deeper into the soil where it is less susceptible to volatilisation losses. However, at low precipitation levels urea remains on the soil surface where it increases both the pH and the NH_3 concentration of surface solution leading to rapid volatilisation losses (Holcomb et al. 2011; Forrestal et al. 2016); (2) soil pH, a soil with a higher pH will be more susceptible to volatilisation losses (Ferguson et al. 1983). Although, Harrison and Webb (2001) suggest that the increase in pH around the urea prill, caused by hydrolysis, negates the effect of soil pH. These factors differed between sites (Table 1) with soil pH of 6.3 and 5.8 at HF and NW respectively. At NW, precipitation in the three days following the first and second N addition exceeded 14.6 mm, potentially reducing NH_3 emissions due to transportation of U into the soil. Whereas at HF, precipitation in the three days following all N applications remained below 7 mm (see supplementary online material Figure S1). Consequently, urea may have remained on the soil surface where it would have been more susceptible to volatilisation losses (Ferguson et al. 1983; Holcomb et al. 2011). The magnitude of the NH_3 emissions at HF from the second N application (72.8 % of applied N) may appear to be exceptionally large but are not without precedent in the literature (Chambers and Dampney 2009, Forrestal et al. 2016). Forrestal et al. (2016) attributed large NH_3 losses following U application to a lack of rainfall and high humidity levels (87%) on the days of application. These factors would have promoted rapid hydrolysis of the urea granule on the grassland surface.

In this study, the use of IU reduced emissions of NH_3 by 48 – 65% relative to U. Inclusion of the urease inhibitor NBPT with urea has also been shown to reduce NH_3 emissions relative to U within the literature (by 73% for winter cereals, and 85% for grassland, Chambers and Dampney 2009; 73 and 84% at two grassland sites, Forrestal et al. 2016). Consequently, we accept the hypothesis that IU fertiliser can reduce NH_3 emissions relative to U fertiliser.

N_2O emissions

Nitrous oxide emissions contributed substantially less to the gaseous N losses than NH_3, ranging 0 - 0.6% of N applied. The greatest N_2O emissions were observed at NW under AN during the first N application. In contrast to NH_3 volatilisation, denitrification is enhanced under anaerobic conditions (Bremner 1997). Therefore, the rainfall that followed the first N application concomitant with WFPS of ~80% (supplementary online information Figure S2) and the readily available NO_3^- source (supplementary online information Figure S3), provided optimal conditions for N_2O emissions to rapidly follow AN application (Clayton et al. 1997; Skiba and Smith 2000; Smith et al. 2012). Although IU significantly reduced NH_3 emissions relative to U, it may have led to pollution swapping with increased (although non-significant) mean N_2O emissions from IU at both sites than from U. Thus, we can tentatively accept the hypothesis that reductions in NH_3 emissions caused by the IU treatment led to increased N availability for additional N loss pathways, in this case via N_2O.

In this study, we have shown how local environmental conditions can exacerbate N losses via one pathway, whilst reducing them for another (the NH_3 and N_2O losses for NW following the first N application; ~~Figs~~Figures~~.~~ 3 and 4). These interrelations were described by Brink et al. (2005), whereby NH_3 emission abatement led to increased N_2O emissions across Europe.

Therefore, attempts to mitigate N losses must prioritise the N loss with the greatest impacts, which in the case of our study was NH_3.

Economic and externality implications of N fertiliser choice

The decision to favour U fertiliser is typically an economic one, reflecting the low N purchase price relative to AN and IU. Here we present data demonstrating that the cost of N from U is greater if N losses of NH_3 and N_2O are incorporated, increasing from a purchase cost of € 0.69 to an effective fertiliser cost of € 0.87 - 1.19 kg N^{-1}. The varying cost is dependent on gaseous N losses in the forms NH_3 and N_2O, and would be greater still if N_2 and NO losses had been measured and included. At the HF site, this led to the U treatment having the greatest effective fertiliser cost at 1.19 € kg N^{-1} of the three N sources examined. Although at NW, U remained the cheapest effective externality fertiliser cost even with an increase from original N fertiliser cost of 0.18 € kg N^{-1}, compared to price increases of 0.05 and 0.07 € kg N^{-1} for IU and AN. However, the effective fertiliser cost calculation only includes direct economic costs through N losses. Once N losses (as kg N^{-1} applied) are put into the wider societal context, with the cost of N pollution on society (see Brink and van Grinsven 2011), we can derive the effective externality fertiliser cost (Table 2). Although externality costs associated with N losses from agricultural land contain inherent uncertainties (linked to the values different communities will place on N benefits and costs; Brink and van Grinsven 2011), we consider them a useful method for considering wider impacts of N use. Including externality costs into the unit cost of the fertiliser resulted in large increases, especially for U which increased from 0.69 to 11.3 € ~~/~~kg N^{-1}. As such, we can accept our last hypothesis, that externality costs would be greatest from the U fertiliser. These costs are largely driven by the impacts to human health of NH_3, the contribution N_2O makes toward climate change, and wider environmental damage through loss of ecosystem services and biodiversity (Brink and van Grinsven 2011). It is essential to consider the wider costs of agricultural practices and management decisions to society, although with the increasing importance of stability in food security, it is more difficult to reach conclusions on how to pay for these costs.

Conclusions

The N loss pathways examined here suggest that for the farmer, economic losses associated with N use efficiency are greatest when using urea fertiliser relative to ammonium nitrate or urea with NBPT. The urea with NBPT treatment reduced NH_3 emissions by 48 - 65% relative to the urea treatment. However, as no yield effect was observed for urea at these two study sites, it would remain an attractive cost-effective choice despite the large gaseous emissions. When the costs to society and the environment were included into the fertiliser cost of N, urea clearly presents a non-economically viable N source, whereas ammonium nitrate and urea with NBPT had substantially lower effective externality fertiliser costs. Consequently, there may be a need for the externality costs that society pays, to be incorporated within the N unit cost to encourage uptake of N fertilisers with less adverse impact.

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Table 1. Background soil properties at the Henfaes (HF) and North Wyke (NW) sites. Values represent means ± ~~SE~~ standard error (*n* = 4).

Table 2. N budget for silage production and externality costs of gaseous N losses. Including: N fertiliser inputs, N offtake as herbage, gaseous losses (losses from the C treatment subtracted) of NH_3 and N_2O and calculation of effective fertiliser cost at the two grassland sites (HF and NW). Externality costs (€ ha^{-1}) of gaseous N losses (NH_3 and N_2O) from N fertiliser addition used to calculate effective externality fertiliser cost (€ kg N^{-1}) for the ~~2~~ two grassland sites (HF and NW). Externality costs taken from the European Nitrogen Assessment (Brink and van Grinsven, 2011). An NH_3 emission rate of 1.3% was applied to the AN treatment for the HF site (European Environment Agency 2016).

Figure 1. Herbage dry matter yields for each silage cut relating to N applications 1, 2 and 3 at the Henfaes and North Wyke field sites. Where AN is ammonium nitrate, U is urea, IU is inhibited urea, and C is the 0N control. Bars are mean values (*n* = 4), ± standard error of mean. Letters above error bars indicate significant differences in dry matter yield between treatment within each N application and field site.

Figure 2. Herbage quality indices for each silage cut relating to N applications 1, 2 and 3 at the Henfaes and North Wyke field sites. Bars represent mean values (*n* = 4), ± standard error of mean. Letters above error bars indicate significant differences in ~~dry matter yield~~herbage quality between treatment within each N application and field site.

Figure 3. Cumulative NH_3 emissions, measured over 21 days following each N application, at Henfaes and North Wyke. At North Wyke bars represent mean values (*n* = 4), ± standard error of mean. At Henfaes bars represent mean values (*n* = 3 for N application 1, and *n* = 4 for N applications 2 and 3), ± standard error of mean. Letters above error bars indicate significant differences in ~~dry matter yield~~cumulative NH_3 emissions between treatment within each N application and field site.

Figure 4. Cumulative N_2O emissions, following each N application, at Henfaes and North Wyke. Where AN is ammonium nitrate, U is urea, IU is inhibited urea, and C is the 0N control. At Henfaes a combination of static manual and automated N_2O sampling chambers were used, consequently following N application 1, static chambers were only used on the C treatments and automated chambers were used for the different N treatments ($n = 4$). Whereas, following N applications 2 and 3 the static chambers were removed and automated chambers were spread across all treatments, therefore $n = 3$. Error bars represent ± standard error of mean. At North Wyke N_2O emissions were determined using the static manual chamber technique and bars represent mean values ($n = 4$), ± standard error of mean. Letters above error bars indicate significant differences in ~~dry matter yield~~cumulative N_2O emissions between treatment within each N application and field site.