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# *Interactive comment on* "Nitrogen use efficiency and $N_2O$ and $NH_3$ losses attributed to three fertiliser types applied to an intensively managed silage crop" *by* Nicholas Cowan et al.

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Dear reviewer 1, We would like to thank you for your extensive comments and suggestions on our original manuscript which you have clearly invested some time. We have made edits in our original manuscript based on these comments and suggestions, and we hope that our corrections and replies are satisfactory (See attached supplement file for clerer formatting of reply).

In response to reviewer 1 First, the motivation is unclear. The authors argue that urease inhibitors might not only decrease NH3 emissions but also increase N2O emissions compared to untreated urea. It is not explained by what mechanism this



would occur. Text added to intro: 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 NH4+ to NO3- in soils results in a decrease in N2O at the expense of an increase in NH3 volatilisation (Lam et al., 2016; Zaman et al., 2009). In theory, the use of a urease inhibitor should reduce both the emission of NH3 by reducing the rate at which urea is converted to NH4+ 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 two main N2O producing processes of nitrification and denitrification use NH4+ and NO3- as substrates and consequently also depend on urea hydrolysis. Urease inhibitors should therefore rather decrease than increase N2O emissions. The reference cited by the authors (Lam et al., 2017) does also not mention a potential increase in N2O release by urease inhibitors, but in contrast discusses a potential increase in NH3 release by nitrification inhibitors that are designed to reduce N2O emissions. The reviewer is correct in that theoretically the urease inhibitors should reduce N2O emissions by limiting the rate of available nitrogen in the soil released from the fertiliser, which was the reason for the field testing in this study. But there are many unknowns when it comes to the application of these inhibitors, especially as N2O emissions are so unpredictable and yields may be affected. We cite the Lam et al., 2017 paper as a relevant example of the potential negative aspects of the addition of a type of inhibitor which is often mentioned in discussions surrounding the uncertain impacts of chemical additives to traditional fertilisers, albeit a fundamentally different one used in this study. We have added text to the introduction and discussion sections to address the reviewers concerns. In addition, I am wondering about long-term effects of the urease inhibitor on NH3 fluxes. NH3 was measured over 14 days after fertilization (in contrast to a 30-day period for N2O – why?). No increase in plant N yield was observed by the inhibitor treated urea compared to untreated urea and on average

55% of the applied fertilizer was accounted for in the experiments. Is it possible that a large fraction of the inhibited urea remained in the soil and will eventually release NH3 once the (short-term) inhibitor stops working? The short-term nature of the experiment is briefly mentioned in the conclusions, but the resulting limitations should be discussed more thoroughly. The two week measurement period of NH3 was based on the methodology and funding we had available. Extending this period was not possible, nor do we believe it was necessary. The measurements show that NH3 emission reduced exponentially to near zero (or uptake) by the time two weeks had passed in all cases. Due to the limits of detection of NH3 measurement methodology, proceeding longer than 2 weeks would not have provided any data of use. As the harvests were only approximately 1 month apart, if there had been residual nitrogen in the soil we would have observed an increase in yield, nitrogen content of the soil or emissions from the treated urea plots in the following harvest. On all occasions the soil nitrogen content was similar to the surrounding plots, indicating that there was no significant quantities of residual N. Text added to method section: 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 NH3 flux measurements, and numerous studies of NH3 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. I further find the introduction and discussion of previous studies on the effect of urease inhibitors on plant yields, NH3 and N2O emissions rather shallow (e.g., introduction in lines 83-88, rare mentioning of previous work in the discussion). A range of papers have been published on the topic, e.g. recently Graham et al. (2018, Soil Science Society of America Journal), as well as multiple papers by Zaman et al. Graham manuscript is behind a paywall, but further references and text has been added to introduction and discussion sections. Added to introduction: This is most commonly observed for nitrification inhibitors in which the slowing on the



conversion of NH4+ to NO3- in soils results in a decrease in N2O at the expense of an increase in NH3 volatilisation (Lam et al., 2016; Zaman et al., 2009). In theory, the use of a urease inhibitor should reduce both the emission of NH3 by reducing the rate at which urease is converted to NH4+ in soils, thus limiting available nitrogen in all forms. This may however, limit the rate at which crops also receive Nr and reduce yields. Added to discussion: Previous studies highlight a potential for pollution swapping with nitrification inhibitor treated urea (typically dicyandiamide, a.k.a. DCD), suggesting that a reduction in NH3 emissions results in a higher N2O production (Lam et al. 2016). that by reducing the rate of conversion of NH4+ to NO3- in soils that NH3 emissions are increased (Lam et al., 2016; Zaman et al., 2009). Elevated N2O and NH3 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 N2O and NH3 emissions. Previous studies have shown that the use of urease inhibitors can significantly reduce N2O emissions (Singh et al., 2013; Zaman et al., 2009). Line 34-35: Are the mentioned reductions by 90% and 47% or did the reduced values correspond to 90% and 47% of the comparison value? Text reworded to make it clearer: “The urea coated with a urease inhibitor did not significantly increase yields; however, ammonia emissions were only 10 % of the magnitude measured for the uncoated urea, and N2O emissions were only 47 % of the magnitude of those measured for ammonium nitrate fertiliser.” Line 42: Please add examples of agriculturally important Nr forms. Text changed: 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). Lines 48-51: I suggest to change the sequence of this sentence, first introducing different pathways of N loss to link to the sentence before, and then mention the resulting environmental damage. Text changed: 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 (NO3-) run-off into streams and waterways (Lu and Tian 2017) as well as gaseous losses in the form of ammonia (NH3) (Bouwman et al., 1997), nitrous oxide (N2O) (Reay et al., 2012), and nitrogen oxides (NOx) (Bertram et al. 2005). This relatively low nitrogen use efficiency (NUE) results in significant environmental damage at a global scale. Line 62: Do you mean an increase in rates of fertilizer application? Please also add a reference to support this projection. Added reference FAO, 2017 Line 90-93: Please rephrase this sentence. It is unnecessarily complicated and contains the word "required" three times. Text changed: Further work using specific products in different environments is needed to supply the evidence that will provide the agricultural community with the confidence to make the changes required to meet future NUE demands globally. Lines 98-100: I am not sure I understand. Do you mean that the study area is representative for agriculturally used grasslands in the UK? Please clarify. I have changed the text slightly to make it clear that the experiment aims to represent conditions in the UK: 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 km2) 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. Lines 115-118: Please add some details to the description of the two fields. Are exposure, slopes, soil types etc. similar? Is grazing/mowing history similar? Anything else that might affect the results? I also suggest to move the different pH values presented in the paragraph below here. Text changed to: The soil in both fields is classified as a clay loam for the top 30 cm in fields, with a pH (in H2O) 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 Rowan-hill 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. Lines 138-140: How were these parameters measured? See above Line 142-144: Considering the high variability between replicates and often similar values of control and treatment plots, how did you treat uncertainties in this calculation and in others? Text added: 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. Line 261: Measurements of soil moisture and soil temperature are mentioned here but not presented in the manuscript. Soil moisture data in particular would be a good complement to the manuscript, for instance for interpreting the observed N2O fluxes. The reviewer is correct in that soil moisture measurements are typically used to help describe N2O fluxes, but we found no statistical correlation with N2O flux and soil moisture in this experiment in any of the fertiliser applications. Due to the already long length of the manuscript we decided to cut this out as is provided no additional explanation for variations in observed fluxes. We have now removed the text describing the measurements. Line 268: Considering the discussed large variability of measured parameters, please present uncertainty estimates (e.g., standard deviation) together with the averages throughout the Results section. Corrected Line 273: How can meteorological conditions be ruled out as the reason behind the observed differences between the two fields in the two years? If site properties lie behind the differences, what specific properties could that be (e.g., are there differences in N availability to start with)? Also, in what sense was the 2016 yield "exceptional" – compared to 2017, or compared to the usually observed yield in such systems? Text changed to clarify: 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. Line 288: Are the values after subtraction of the background? Text added: (after subtraction of the control) Lines 292-293: I find it hard to see to see a consistent pattern of overall later peaks in the urea than the Nitram treatments. Elevated fluxes can be seen after 10 days for the urea and treated urea in Figure 2. Text changed to clarify: Fluxes also increased after the urea and inhibitor coated urea applications, although the timing of the peaks in these emissions were more variable than those observed from the Nitram plots. Line 309: Are these values after the subtraction of the background? Also, why was the measurement period for NH3 shorter than for N2O? Text changed to: In four of the five events, Nitram was the highest N2O emitting fertilizer of the treatments after 30 days (minus background from control plots) with a mean EF between. . . As discussed previously, the FIDES method was only carried out for 2 weeks for logistical and methodological reasons (see text added in 2.4). Lines 308-309 and 314-315: These sentences have considerable overlap; please restructure. Text changed to: Differences in NH3 from individual plots was typically larger than an order of magnitude of the mean value of the grouped treatments. Lines 331-333: It looks more like an additional peak in NH4+ concentrations; there is also a peak in the beginning of similar magnitude than for the other events. I believe that the additional peak in NH4+ concentrations shows a delay in urea hydrolysis. The peak in the other events is there as it is not delayed, as stated in the original text. Line 334: What do you mean with variation on a log-normal scale? Log-normal distributions are a common statistical phenomenon that we do not feel is necessary to describe in the text. We have re-worded the text to clarify. Text changed to: Concentrations of NO3- followed a log-normal distribution in a similar fashion to the NH4+ concentrations. Line 339: Differences between sites and years cannot be distinguished in this setup; please rephrase accordingly. Text removed Line 353-355: Were the 2017 plots not grazed by sheep before? Please add potential differences in



grazing history and intensity to the site description in the Material & Methods section. Text added to method section: 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. Lines 357-359: With the scaling of the y-axes of Figure 4, it is almost impossible to compare initial ammonium and nitrate concentrations between fertilization events. It would help to present control concentrations here again to support the claimed differences in initial Nr concentrations between events. I can understand the reviewer's frustration with this figure, but due to the log-normal distribution of the data, it is exceptionally difficult to present the data in a clear manner in any format. I disagree that it is not possible to compare the starting N in the treatments as it is clear from the Control column (LHS) that nitrogen in the soil is consistently at about 10 - 40 mg N kg-1 for the different events. We have tried to present this data in a variety of ways, and believe that changing its current format would cause more problems than it solves. Line 375: The Lam et al. 2017 reference does not indicate that a reduction in NH3 emissions might result in higher N2O production – the paper is about nitrification inhibitors and a potential increase in NH3 emissions that follows reduced N2O emissions. The reviewer is correct in this statement. We have altered the text to include more relevant comparisons with literature. Text changed to: 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 NH4+ to NO3- in soils that NH3 emissions are increased (Lam et al., 2016; Zaman et al., 2009). Elevated N2O and NH3 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 N2O and NH3 emissions. Previous studies have shown that the use of urease inhibitors can significantly reduce N2O 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). Line 392: Does the accounted for Nr include measured ammonium and nitrate, additional N in the harvested plants, as well as NH3 and N2O emissions? Please specify. Considering that no increase in plant N yield was observed by urease inhibitor compared to untreated urea and the short duration of the NH3 flux measurements, is it possible that a large fraction of the inhibitor-treated urea still remains in the soil at the end of the experiment and will eventually release NH3 once the (short-term) inhibitor stops working? Text changed to: After the N content of the crop, the N content of the soil and emissions of N2O and NH3 are taken into account, the majority (> 55 %) of applied Nr in the experiments remains unaccounted for by the time of harvest. As discussed previously, the NH3 emissions have declined to near zero after 2 weeks and it is unlikely that emission is statistically significant compared to deposition. See text added to section 2.4. Tables 2, 3, 4: Considering the high variability within treatments, please add information on whether differences between treatments (in particular also between background and fertilizer NH3 and N2O fluxes) were statistically significant. As the standard deviations are presented in the table, and the number of data points for each replication is relatively low (n = 4) and often the data follows a log-normal distribution, I do not believe that individual significance tests offer much in the way of describing the data beyond what is already presented. The significance values for the important comparisons are presented in the text. Figure 1: It might help to indicate the experimental periods (fertilizer addition and run time of flux measurements). Text added to figure caption: Fertiliser was applied at t = 0 days, and the measurements lasted up to 30 days for each event. Line 25: The first “and” is superfluous. Corrected Line 32: The abbreviation “Nr” has not been introduced yet. Corrected Lines 33-34: “The urea coated with a urease inhibitor did not significantly increase yields” – compared to what treatment? Corrected Line 71: Add “to” before “convert”. Corrected Line 73: Add “N” after “less”. Corrected Line 77: Change “trialed” to “tested”. Corrected Line 83: Typo, this should be “losses”. Are the losses quantified in these studies in



the form of NH3, N2O or both? Corrected Line 87-88: I suggest “. . . reduction of one form of Nr pollution may contribute to increase another”. Corrected Line 147: Please change to “for both 2016 and 2017 experiments” or similar; the sentence gives the impression of measurements throughout the entire growing season of multiple years. Corrected Line 149: “a sealed lid” Corrected Line 238: “several” Corrected Line 239: “holds” and “centre” Corrected Line 253: “to provide” Corrected Line 335: Do you mean gaseous NH3 or NH4+ in the soil solution? Corrected Line 345: Change “was” to “were”. Corrected Lines 348-349: Please add uncertainties. Corrected Line 350: Typo, should be “trials”. Corrected Line 353: Why “although”? Changed Line 358: “show” Corrected Line 365: Change to “under the conditions”. Corrected Line 368: “the treatment effect” Corrected Line 382: FIDES is the mathematical approach, not the measurement method. Changed Line 386: Change to “. . . while Nitram treatments do not . . .”. Changed Line 399: Add “of” before “applied”. Corrected Line 402: “under the right conditions”. Also, which conditions would be “right”? Changed text to: . . .and microbial emissions of NO and N2 can account for Nr losses of an order of magnitude higher than N2O when water filled pore space (WFPS) is particularly low (< 40 %) or high (> 80 %) (Davidson 1993; Weier 1993). Line 410: Change “emitters” to singular. Corrected Line 413: Please specify that this decrease is by 90%, not to a level of 90%. Corrected Figure 2: The headers are not consistent with the other figures (Ammonium Nitrate instead of Nitram). Corrected

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2019-90/bg-2019-90-AC1-supplement.pdf

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2019-90, 2019.