



TITLE Ammonia emissions from urea, stabilized urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland

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1 **Title: Ammonia emissions from urea, stabilised urea and calcium ammonium nitrate:**  
2 **insights into loss abatement in temperate grassland**

3

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16 **Short running head title:** Ammonia emissions from fertilisers

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19

20 **Abstract**

21 Fertiliser nitrogen (N) contributes to ammonia (NH<sub>3</sub>) emissions, which European Union  
22 member states have committed to reduce. This study evaluated NH<sub>3</sub>-N loss from a suite of N  
23 fertilisers over multiple applications, and on gaining insights into the temporal and seasonal  
24 patterns of NH<sub>3</sub>-N loss from urea in Irish temperate grassland using wind tunnels. The  
25 fertilisers evaluated were: calcium ammonium nitrate (CAN), urea, and urea with the N  
26 stabilisers N-(n-butyl) thiophosphoric triamide (NBPT), dicyandiamide (DCD), DCD+NBPT,  
27 and a maleic and itaconic acid polymer (MIP). 200 (and 400 for urea only) kg N/ha/yr was  
28 applied in five equal applications over the growing season at two grassland sites (one for  
29 MIP). Mean NH<sub>3</sub>-N losses from CAN were 85% lower than urea which had highly variable  
30 loss (range 45% points). The effect of DCD on NH<sub>3</sub> emissions was variable. MIP did not  
31 decrease loss but NBPT caused a 78.5% reduction, and when combined with DCD, a 74%  
32 reduction compared with urea alone. Mean spring and summer losses from urea were similar,  
33 although spring losses were more variable with both the lowest and highest loss levels.  
34 Maximum NH<sub>3</sub>-N loss usually occurred on the second day after application. These data  
35 highlight the potential of stabilised urea to alter urea NH<sub>3</sub>-N loss outcomes in temperate  
36 grassland, the need for caution when using season as a loss risk guide and that urea  
37 hydrolysis and NH<sub>3</sub>-N loss in temperate grassland is rapid. Micrometeorological  
38 measurements focused specifically on urea are needed to determine absolute NH<sub>3</sub>-N loss  
39 levels in Irish temperate grassland.

40

41 **Key words:** ammonia, volatilisation, urea, ammonium nitrate, inhibitors, grassland, fertiliser

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43

## 44 **Introduction**

45           Global ammonia (NH<sub>3</sub>) emissions from fertiliser nitrogen (N) are estimated at 10 to  
46 12 Tg N/yr (Beusen *et al.*, 2008). These emissions are of concern from economic,  
47 environmental, and national policy perspectives. As addition of supplemental fertiliser N is a  
48 cornerstone of many agricultural systems N lost as NH<sub>3</sub>-N must be replaced, typically at an  
49 economic and environmental cost, in order to sustain agro-ecosystem productivity. Ammonia  
50 lost from agricultural systems may be re-deposited contributing to eutrophication and  
51 acidification of terrestrial and aquatic ecosystems (Sutton *et al.* 1992) and indirect emissions  
52 of nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas. In terms of national policy, EU member  
53 states have committed to reducing NH<sub>3</sub>-N emissions under the National Emissions Ceiling  
54 Directive (EU, 2001).

55           The use of urea in place of ammonium nitrate-based fertiliser has some potential for  
56 mitigating fertiliser N related N<sub>2</sub>O emissions (Dobbie & Smith, 2003). However, urea is  
57 vulnerable to NH<sub>3</sub> volatilisation (Chambers & Dampney 2009). Promisingly N stabilised  
58 using N inhibitors can play a role in mitigating losses of NH<sub>3</sub>-N (Watson *et al.*, 2009), N<sub>2</sub>O  
59 (Di *et al.*, 2007) and nitrate leaching (Dennis *et al.* 2012). These inhibitors can be divided into  
60 two groups: i) urease inhibitors and ii) nitrification inhibitors. Urease inhibitors reduce NH<sub>3</sub>  
61 volatilisation from urea by inhibiting the enzyme urease which catalyses urea hydrolysis. The  
62 urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (NBPT) has been shown to reduce NH<sub>3</sub>  
63 loss from urea (Watson *et al.*, 1990, 1994; Goos *et al.*, 2013). The maleic and itaconic acid  
64 polymer (MIP) has been marketed globally and claims to be a urease and a nitrification  
65 inhibitor. However, a number of studies (Franzen *et al.*, 2011; Goos *et al.*, 2013) have shown  
66 that urea treated with MIP did not reduce NH<sub>3</sub> loss from urea. Nitrification inhibitors, such as  
67 dicyandiamide (DCD), inhibit ammonia monooxygenase, which catalyses oxidation of  
68 ammonium (NH<sub>4</sub><sup>+</sup>) to nitrite (Kim *et al.* 2012). Although effective for reducing N<sub>2</sub>O

69 emissions and leaching, nitrification inhibitors may increase NH<sub>3</sub> emissions. In a meta-  
70 analysis, Kim *et al.* (2012) reported that the effect of DCD on NH<sub>3</sub> emissions was  
71 inconsistent, with increased NH<sub>3</sub> emissions in 26 studies, no change in 14 studies and  
72 decreased emissions in 6 studies. They linked nitrification inhibitor related increases in NH<sub>3</sub>  
73 loss to increasing soil pH and decreasing cation exchange capacity (CEC).

74 Previous studies have evaluated NH<sub>3</sub> loss from urea and urea with inhibitors,  
75 particularly in cropping systems; however field measurements in temperate grassland are  
76 more limited. To address this knowledge deficit, the current study assessed NH<sub>3</sub>-N loss from  
77 fertiliser formulations with and without N stabilisers over multiple applications.

## 78 **Materials and methods**

### 79 *Site description and experimental design*

80 Experiments were conducted at grassland sites located at Hillsborough (HB), Co.  
81 Down, Northern Ireland (54°46'N; 6°08'W) and Johnstown Castle (JC), Co. Wexford, Ireland  
82 (52°17'N; 6°30'W). Hillsborough is a moderately drained loam classified as a Dystric Umbric  
83 Stagnosol (FAO, 2014) (45% sand, 33% silt, 22% clay, 11% organic matter, pH 5.6, CEC  
84 24.43 cmol<sup>+</sup>/kg). Johnstown Castle is a moderately drained loam classified as a Stagnic  
85 Cambisol (FAO, 2014) (52% sand, 34% silt, 14% clay, 7% organic matter, pH 5.8, CEC  
86 15.46 cmol<sup>+</sup>/kg). Swards were dominated by perennial ryegrass (*Lolium perenne* L.).  
87 Precipitation, ambient and soil temperature were measured by a meteorological station (ca.  
88 500 m from the study site). A HH2 moisture meter (Delta Devices, Burwell, Cambridge,  
89 England) was used to measure soil volumetric moisture content on site.  
90 Fertiliser treatments were applied in five equal split applications. Treatments were CAN,  
91 urea, urea+NBPT, urea+DCD, urea+NBPT+DCD and at JC only urea+MIP. All treatments  
92 were applied at 200 kg N/ha and both sites also included a urea 400 kg N/ha/yr treatment.

93 The source of the urease inhibitor NBPT was Agrotain® which was coated onto urea  
94 granules at 660 ppm NBPT (on a urea weight basis). Koch Agronomic Services supplied the  
95 urea+DCD granules, where DCD had been added to urea at the molten stage at the rate of  
96 3.5% on a urea-N basis. Urea+DCD granules were coated with Agrotain® on site to make  
97 urea+NBPT+DCD. The source of MIP was commercially available urea treated with  
98 Nutrisphere®. A randomised block design with three replicates was used except for the urea  
99 400 kg N/ha/yr and urea+MIP treatments at JC, each of which had two replicates. Fertiliser  
100 treatments were applied between March and September 2014 (Figures 1 and 2).

#### 101 *Ammonia measurements*

102 Ammonia loss from the treatments was measured using a system of wind tunnels  
103 similar in design to Lockyer (1984) and Meisinger *et al.* (2001). In brief, each wind tunnel  
104 unit consisted of a 0.5 m x 2 m polycarbonate canopy with an integrated inlet air sampling  
105 line, an axial fan to draw air through the canopy, an anemometer to measure air speed, which  
106 was 0.9 to 1.0 m/s at the anemometer, and an outlet air sampling line. A control box housed a  
107 diaphragm pump for air sampling, a flow meter and a critical orifice for both air sampling  
108 lines. Inlet and outlet air NH<sub>3</sub>-N was measured by passing through individual conical flasks  
109 containing 100 ml of 0.02 M orthophosphoric acid. If the difference in concentration between  
110 the inlet and outlet acid trap was negative the loss was set to zero. The NH<sub>3</sub>-N flux rate was  
111 calculated by dividing the emission by the exposure time.

112 Measurements were conducted for between 14 and 19 days following each fertiliser  
113 application (Figure 1 and 2) and in all cases until NH<sub>3</sub>-N emissions had returned to  
114 background levels. Each plot (2.5 m by 2.5 m) could accommodate wind tunnel moves  
115 sequentially through three positions on each acid trap change occasion to minimise  
116 interference of the wind tunnel canopy on precipitation reaching the plots. The fourth move  
117 returned the wind tunnel to its starting position. Acid solutions were changed at each wind

118 tunnel move and  $\text{NH}_4^+$ -N content was determined colorimetrically using a QuAAtro 3 (Seal  
119 Analytical, Fareham, U.K.) at HB and an Aquakem 600A Analyser (Thermo Electron OY,  
120 Vantaa, Finland) at JC.

### 121 *Data analysis and interpretation*

122 The acid trap change period varied during the study, consequently the time-integrated  
123 hourly flux (g N/ha/hr) (Engel *et al.*, 2011) is presented with the flux indicated at the mid-  
124 point of the sampling period in Figures 1 and 2. A repeated measures analysis of variance  
125 was conducted for both i) the time-integrated flux of  $\text{NH}_3$ -N and ii) the percentage  $\text{NH}_3$ -N  
126 loss using the PROC MIXED procedure of SAS (2002-2010, SAS Institute Inc., Cary, NC,  
127 U.S.A.). The sources of variation in the model were time (of sampling in the case of time-  
128 integrated  $\text{NH}_3$ -N flux or application date in the case of per application loss) and fertiliser N  
129 treatment. A generalised linear mixed modelling approach was used to test for a fertiliser N  
130 treatment effect on annual  $\text{NH}_3$ -N loss using the PROC GLIMMIX procedure of SAS 9.3.  
131 Differences between fertiliser treatments were determined using the F-protected least  
132 significant difference (LSD) test at the 95% confidence level.

## 133 **Results and discussion**

### 134 *Ammonia loss from CAN and urea*

135 The mean  $\text{NH}_3$ -N loss from CAN of 4.2% was higher than the mean emission of 0.8%  
136 reported by Black *et al.* (1985). Higher losses from CAN in the present study may be partially  
137 attributable to more rapid dissolution of the calcium carbonate ( $\text{CaCO}_3$ ) in CAN, which  
138 causes a small initial rise in soil pH around the granule (Black *et al.*, 1985). In contrast, the  
139 average loss from urea was much higher at 25.1% for HB and 30.6% for JC and spanned a  
140 wide range (7.5 to 52.8%) across the five 40 kg N/ha applications. While these average

141 values are similar to the 30% reported by Chambers & Dampney (2009) in UK grassland,  
142 also using wind tunnels, they are much higher than those of Black *et al.* (1985) who reported  
143 average loss over four seasons of 11.9% for urea. Black *et al.* (1985) state that, due to the  
144 measurement method these losses were likely near the upper limit for grassland in  
145 Canterbury, New Zealand. Similarly, we suspect that the losses recorded by the wind tunnels  
146 in the current study are at the upper limit of losses for Irish temperate grassland. One reason  
147 is that in a parallel study (Harty *et al.*, 2015) there were similar apparent N fertiliser  
148 recoveries in herbage of 65% for CAN and 60% for urea. Also the average urea-N losses of  
149 25.1 to 30.6% are similar to the 27% loss measured by Schwenke *et al.* (2014) from urea  
150 applied on neutral to alkaline grassland with limited or no precipitation for two weeks after  
151 application, conditions expected to promote NH<sub>3</sub>-N loss. Our sites were acidic (pH 5.6 at JC  
152 and 5.8 at HB) and significant precipitation was a feature of many periods following fertiliser  
153 application. It is known that NH<sub>3</sub>-N losses measured by wind tunnels can differ from  
154 integrated horizontal flux (IHF) because wind tunnels interfere with wind speed and  
155 precipitation in particular. Schwenke *et al.* (2014) used the IHF micrometeorological  
156 approach. Ryden & Lockyer (1985) demonstrated that where precipitation was not a factor,  
157 urea NH<sub>3</sub>-N loss measured by wind tunnels differed from a micrometeorological approach  
158 when the wind speed difference between the wind tunnel canopy and external conditions  
159 varied by >20%. Additionally, Ryden & Lockyer (1985) found that wind tunnels can  
160 overestimate NH<sub>3</sub>-N losses by a factor of 2.4 to 6 during periods of rainfall. In the current  
161 study, wind tunnels were moved daily to minimise effects on rainfall although such effects  
162 are potentially not completely excluded. Wind tunnels were chosen for the current study  
163 because they permitted inter-comparison of a large suite of fertilisers in replicate, which  
164 would not have been practical using IHF which requires homogeneous fetch and relatively  
165 large land areas.

166 *Temporal pattern of ammonia loss from urea*

167           The maximum rate of NH<sub>3</sub>-N loss from urea typically occurred on the second day  
168 after urea application (8 out of 10 cases), but in all cases within < 3 days (Figure 1 and 2).  
169 This indicates rapid hydrolysis of urea in Irish temperate grassland, in agreement with  
170 Watson & Miller (1996) who reported that 1.3% of N remained in the urea form in the soil  
171 1.75 days after application. Black *et al.* (1985) also reported a one to three day delay in  
172 maximum loss rate from urea in New Zealand pasture. Grass and thatch is a zone of very high  
173 urease activity, 18 to 30 times higher than the soil (Torello & Wehner, 1983), which  
174 promotes rapid hydrolysis of urea in the presence of adequate moisture. Moisture limitation  
175 can inhibit urea hydrolysis and NH<sub>3</sub>-N loss (Ferguson & Kissel, 1986) however such  
176 limitation is rare in Irish grasslands even in the absence of significant precipitation e.g. JC on  
177 March 10 (Figure 1) and HB on September 8 (Figure 2). In these examples, appreciable NH<sub>3</sub>-  
178 N loss occurred rapidly (within <2 days) although precipitation was limited or absent. Urea is  
179 a hygroscopic substance with a critical relative humidity of 80% at 20°C (Adams and Merz,  
180 1929), a humidity level frequently surpassed in Irish grassland. In the two examples above  
181 mean relative humidity on the days of application was c. 87%. Additionally, dew in the  
182 evening and/or mornings could have provided additional moisture.

183 *Effect of precipitation*

184           Urea granules absorb moisture, therefore hydrolysis and resultant NH<sub>3</sub>-N loss  
185 proceeds quickly with maximum loss rates occurring within 3 days in this Irish temperate  
186 grassland study. Holcomb *et al.* (2011) reported that 14.6 mm irrigation immediately  
187 following application reduced urea NH<sub>3</sub>-N losses by 90% however these levels were not  
188 reached in the present study. The highest precipitation level on the day post application was  
189 5.8 mm on May 6 at HB and the resultant loss was 8% (Table 1), much lower than the

190 average loss of 25.1% at this site. This initial 5.8 mm was followed by daily precipitation of  
191 1.8 to 3.6 mm/day for three days and 11.6 mm on the fifth day. A similar rainfall input of 5.4  
192 mm on July 7 at JC followed by 0.6 mm on the day after produced a loss of 26% (Table 1).  
193 Temperatures were warmer in July than in May, however if NH<sub>3</sub>-N loss reduction only is the  
194 goal, the importance of precipitation approaching 15 mm on the day of application or  
195 sustained lower levels of precipitation over several days is apparent. The trade-off between  
196 NH<sub>3</sub>-N abatement and potential N leaching and/or runoff risk potential requires evaluation.

197         The highest losses occurred after the March 10 application at JC under cool air and  
198 soil temperatures (Figure 1), with peak loss from urea occurring on the third day. There was  
199 little precipitation in the week following March 10, thus loss was not suppressed (Figure 1)  
200 and losses continued at appreciable levels over at least seven days. Similarly, in an incubation  
201 study using Irish soils, McGarry *et al.* (1986) observed high losses at 8°C with maximum loss  
202 > 3 days following application and loss rates remaining high for up to 9-16 days.  
203 Accordingly, large NH<sub>3</sub>-N losses from urea can occur over time in temperate grasslands when  
204 precipitation does not arrest loss even under cooler conditions as was seen following the  
205 March 10 application at JC. This finding is in agreement with Engel *et al.* (2011) who  
206 showed that large NH<sub>3</sub>-N losses can occur from urea applied to wheat stubble in Montana  
207 under cold or frozen conditions.

208         However, the effect of precipitation is not straightforward; McInnes *et al.* (1986)  
209 previously reported that small precipitation inputs enhance rather than suppress loss.  
210 Accordingly the minor precipitation levels observed at JC (<0.3 mm/day) in the week  
211 following March 10 (Figure 1) are likely to have promoted loss, thus at least partially  
212 explaining very high loss at this site. The implication is that the timing, volume, and duration  
213 of precipitation following urea application all affect the influence of precipitation on urea  
214 NH<sub>3</sub>-N loss. While precipitation patterns make this difficult to achieve farmers can maximise

215 suppression of NH<sub>3</sub> loss from urea by applying shortly before the onset of appreciable and  
216 sustained precipitation. Development of more specific guidance based on a larger dataset is  
217 warranted.

### 218 *Seasonality*

219 Traditional advice in Ireland that urea is less vulnerable to loss of NH<sub>3</sub>-N in spring  
220 due to cooler temperatures is supported by the HB data with average loss of 32.3% in  
221 summer and 14.5% in spring. Conversely, the average NH<sub>3</sub>-N loss at the JC site was 25.3% in  
222 summer and 39% in spring. Temperatures (Figure 1 and 2) and soil moisture (Table 1) were  
223 broadly similar between sites in spring yet losses were very different. The notable difference  
224 was the occurrence of almost daily precipitation following urea application at HB in spring  
225 (Figure 2) and the near absence of precipitation in the first two days following application at  
226 JC. The high losses in spring are compatible with McGarry *et al.* (1987) whose laboratory  
227 study using Irish soils showed that appreciable NH<sub>3</sub>-N loss can occur not only from  
228 warm/cool-dry [18/8°C, 35% field capacity (FC)] but even from cool-wet (8°C, 85% FC)  
229 soils. As discussed earlier, important differentiating factors in spring loss outcomes appear to  
230 be time until precipitation onset and precipitation persistence.

231 Previous researchers have also noted that the seasonal effects are not pronounced.  
232 Black *et al.* (1985) noted no marked seasonal pattern of NH<sub>3</sub>-N loss from urea in New  
233 Zealand grassland with 13.1, 15 and 11.2% from a summer, autumn and winter application,  
234 respectively, although there was a slight tendency for lower loss in spring at 10%. We also  
235 observed this slight tendency with average loss of 26.8% in spring and 28% in summer but  
236 spring NH<sub>3</sub>-N losses were more variable (8 to 53%) than summer losses (20 to 33%). What is  
237 clear from this study is that NH<sub>3</sub>-N loss from urea can be a significant issue in both spring  
238 and summer.

240 Nitrification inhibitors can potentially reduce both N<sub>2</sub>O emissions (Smith *et al.*, 2012;  
241 Chen *et al.*, 2010) and nitrate leaching (Di & Cameron, 2005; Díez-López *et al.*, 2008) whilst  
242 increasing plant N use efficiency (Abalos *et al.*, 2014). Nitrification inhibitors may also affect  
243 NH<sub>3</sub>-N loss from urea, although Kim *et al.* (2012) reported that the effect was inconsistent.  
244 The current data show that this is also an issue in temperate grassland, with DCD  
245 significantly increasing NH<sub>3</sub>-N loss at JC at three applications (by 15.8% to 23.9 percentage  
246 points, Table 1) and having no effect at two applications. The cumulative effect was a 36%  
247 increase in NH<sub>3</sub>-N loss attributable to using DCD (Table 2). Aisling *et al.* (2008) reported  
248 that NH<sub>4</sub><sup>+</sup> remains in the soil longer when a nitrification inhibitor is used, with approximately  
249 40% more NH<sub>4</sub><sup>+</sup>-N in the soil one day after application when DCD was used with urea. Fox  
250 & Bandel (1989) suggested that a reduction in nitrification by DCD reduces soil acidification,  
251 thereby prolonging the pH spike caused by hydrolysis, thus increasing the period of NH<sub>3</sub>-N  
252 emission. Gioacchini *et al.* (2002) suggested that maintaining NH<sub>4</sub><sup>+</sup>-N in the soil causes a  
253 priming effect mineralising soil organic N. At JC, there is evidence of a more protracted  
254 period of NH<sub>3</sub>-N loss from the DCD treated urea when losses increased significantly i.e.  
255 following the March 10, April 28 and August 18 applications (Figure 1). A longer duration of  
256 emission from DCD treated urea is compatible with the suggestions that NH<sub>3</sub>-N remains in  
257 the soil for longer and that the soil pH peak is prolonged, although this could not be  
258 confirmed in the current study.

259 In contrast, a significant decrease in NH<sub>3</sub>-N loss in four out of five applications was  
260 observed for urea+DCD at HB, with an annual mean loss reduction of 45% compared with  
261 urea only (Table 2). A meta-analysis by Kim *et al.* (2012) also reported a limited number of  
262 cases where DCD decreased NH<sub>3</sub>-N emissions but the reduction was much lower than that  
263 observed at HB. One possible mechanism may be associated with non-target effects of DCD

264 on the soil nitrogen mineralisation-immobilisation turnover (MIT) at HB. In a field study on  
265 MIT at HB McGeough *et al.* (2014) observed significant but inconsistent effects of DCD on  
266 MIT including net immobilisation of N. Furthermore, Ernfors *et al.* (2014) in a laboratory  
267 study with slurry found that the effects of DCD on MIT varied between soils. Increased net  
268  $\text{NH}_4^+$ -N immobilisation could, therefore be a possible mechanism for reduced  $\text{NH}_3$  loss with  
269 urea+DCD. However, further detailed process studies would be needed to understand this  
270 mechanism. It is clear that use of DCD adds to the  $\text{NH}_3$ -N loss uncertainty associated with  
271 using urea as its effects on loss were so variable. With regard to the non-significant effect of  
272 DCD observed on June 3 and July 7 at JC and on May 6 at HB (Table 1) this was associated  
273 with lower initial peaks in  $\text{NH}_3$ -N loss from urea and the early onset of precipitation.

274 The urease inhibitor NBPT was effective in reducing  $\text{NH}_3$ -N emissions from urea in  
275 nine out of ten split applications (Table 1). For the single application where NBPT did not  
276 produce a significant reduction (May 6 2014 at HB)  $\text{NH}_3$ -N emissions from urea were not  
277 significantly different from CAN because of precipitation following application. Averaged  
278 across the two sites, NBPT reduced  $\text{NH}_3$ -N emissions from urea by 78.5% which is similar to  
279 Chambers & Dampney (2009) who reported an average 77% reduction in UK field studies  
280 and Watson *et al.* (2008) who found on average a 79% reduction in laboratory studies with  
281 granular formulations (at 500 mg/kg NBPT).

282 When the urease inhibitor NBPT was included with urea+DCD,  $\text{NH}_3$ -N losses were  
283 74% lower than for urea (Table 1). This is similar to the 78.5% reduction when the urease  
284 inhibitor was used alone, thus NBPT inclusion with DCD may be a strategy for overcoming  
285 the variable  $\text{NH}_3$ -N loss responses associated with DCD.

286 MIP is a co-polymer of maleic and itaconic acid which is marketed as both a urease  
287 and nitrification inhibitor. It was evaluated at JC only and produced the same loss as urea in

288 four out of five applications and a significantly higher loss following the August 18  
289 application. Averaged over the five applications there was no significant difference in  
290 cumulative  $\text{NH}_3\text{-N}$  loss between urea and urea+MIP. There is little information on the  
291 efficacy of MIP in temperate grassland. However, Goos *et al.* (2013) did not find MIP to be  
292 an effective inhibitor of soil or jack bean urease and a meta-analysis by Chien *et al.* (2014)  
293 found that urea+MIP did not provide a significant average plant yield response above urea.

#### 294 *Implications for ammonia inventories*

295 Firstly, this study has shown that CAN has low and consistent  $\text{NH}_3\text{-N}$  loss across a  
296 range of conditions in temperate grassland (Table 1). Thus dependable estimates of national  
297 loss can be made based on the quantities applied irrespective of season of application or  
298 weather patterns within a given year. Secondly, urea usage brings challenges because its use  
299 in place of CAN will increase national  $\text{NH}_3\text{-N}$  emissions. The calculation of this increase is  
300 not straightforward because urea emissions are strongly influenced by climatic conditions  
301 following application. In the present study,  $\text{NH}_3\text{-N}$  loss from urea varied by 45 percentage  
302 points; moreover weather patterns can affect the volume of urea applied in conditions  
303 favouring loss. Thirdly, an application rate effect on  $\text{NH}_3\text{-N}$  loss from urea may be expected;  
304 in the present study this rate effect was detectable at the 95% confidence level in four out of  
305 ten cases (Table 1). Averaged across application timings, doubling the urea N rate increased  
306 the annual  $\text{NH}_3\text{-N}$  loss rate by 31% and 27% at JC and HB, respectively. Applying a  $\text{NH}_3\text{-N}$   
307 loss factor to the nationally utilised volume of urea, to the exclusion of the rate effect will  
308 introduce added uncertainty to loss estimates. Fourthly, the present study demonstrated that  
309 the  $\text{NH}_3\text{-N}$  abatement potential of NBPT was on average 78.5% when used with urea alone or  
310 74% when used in combination with the nitrification inhibitor DCD and that MIP had no  
311 significant effect on  $\text{NH}_3\text{-N}$  loss. This is important information because the use of urea

312 with/without inhibitors is a potential strategy for reducing national N<sub>2</sub>O emissions which  
313 needs to be implemented without causing large increases in NH<sub>3</sub>-N emissions.

314 Whilst this study using wind tunnels has provided comparative data on ammonia  
315 emissions for a range of fertiliser strategies, there is a lack of quantitative data for urea  
316 applied to temperate Irish grasslands which could be obtained using micrometeorological  
317 techniques. In the context of a national ammonia emission ceiling there is a need to address  
318 this knowledge gap.

319

## 320 **Conclusions**

321 The use of urea poses challenges at both local management and national inventory scales and  
322 will increase ammonia loss compared with CAN. Maximum NH<sub>3</sub>-N loss rates from urea  
323 occur quickly in Irish temperate grassland (within two to three days); consequently, to reduce  
324 loss appreciably, it is desirable to apply urea shortly before sustained precipitation is forecast  
325 where possible. One site had higher losses in spring and the other higher losses in summer  
326 owing to environmental conditions but average losses were similar between seasons,  
327 highlight the importance of having large multi-site databases for generation of general advice.  
328 The urease inhibitor NBPT effectively abates NH<sub>3</sub>-N loss from urea when used with or  
329 without a nitrification inhibitor. This study has provided information on the abatement  
330 potential of a suite of N fertiliser options, however there is an important knowledge gap  
331 regarding absolute levels of NH<sub>3</sub>-N loss from urea in Irish grassland which could be  
332 addressed by a campaign of micrometeorological measurements. Such knowledge is of  
333 critical importance in the context of national commitments to reduce NH<sub>3</sub>-N loss whilst  
334 growing the agri-food sector.

335

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469

470

471 **Table captions**

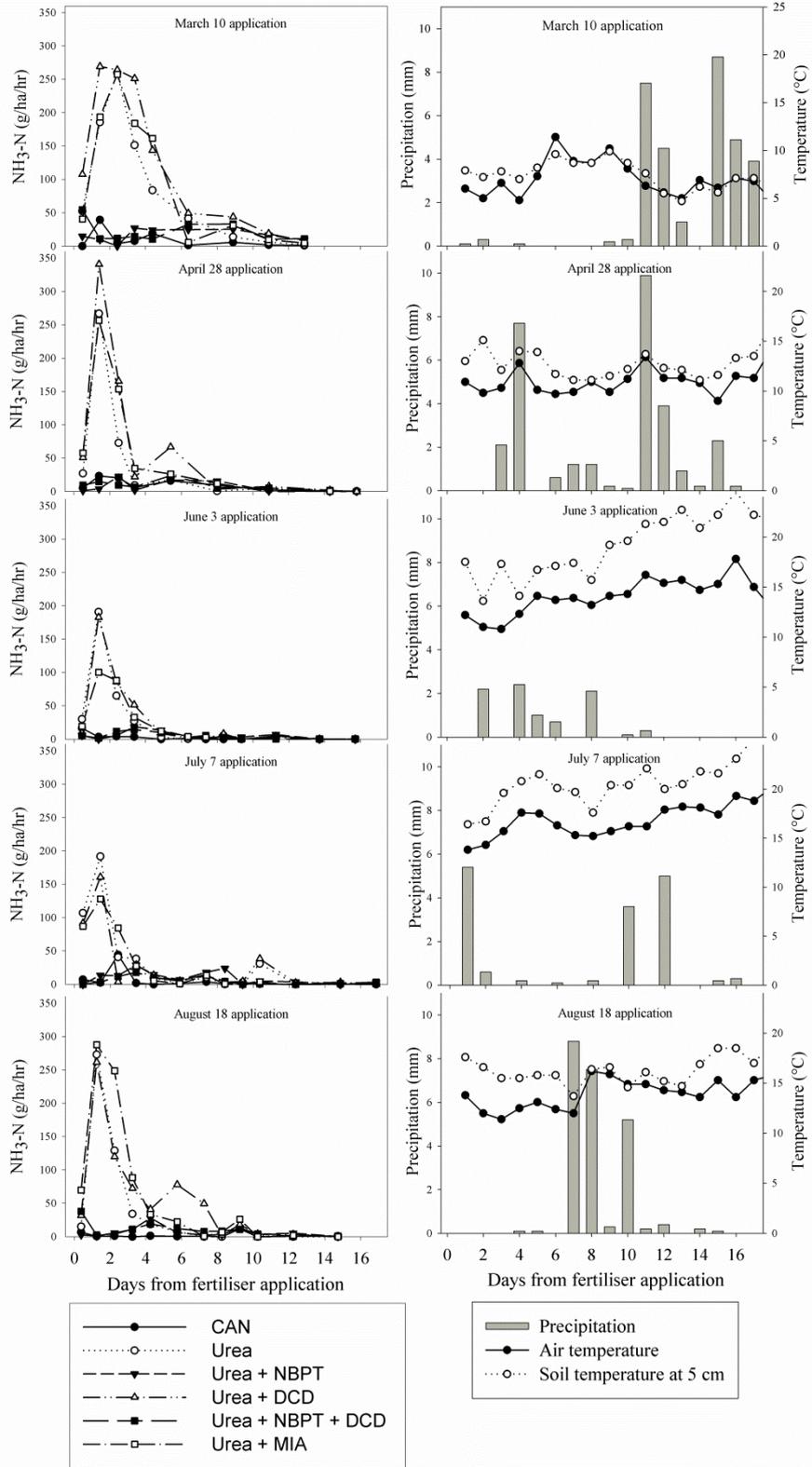
472 Table 1 Ammonia (NH<sub>3</sub>) loss as affected by fertiliser N treatment for each application date at  
473 Johnstown Castle and Hillsborough sites.

474 Table 2 Annual ammonia (NH<sub>3</sub>) loss as measured by wind tunnels and the change (Δ) in loss  
475 compared with the urea 200 kg N/ha rate for the other treatments. N applied to grassland N  
476 input in five equal split applications (40 or 80 kg N/ha).

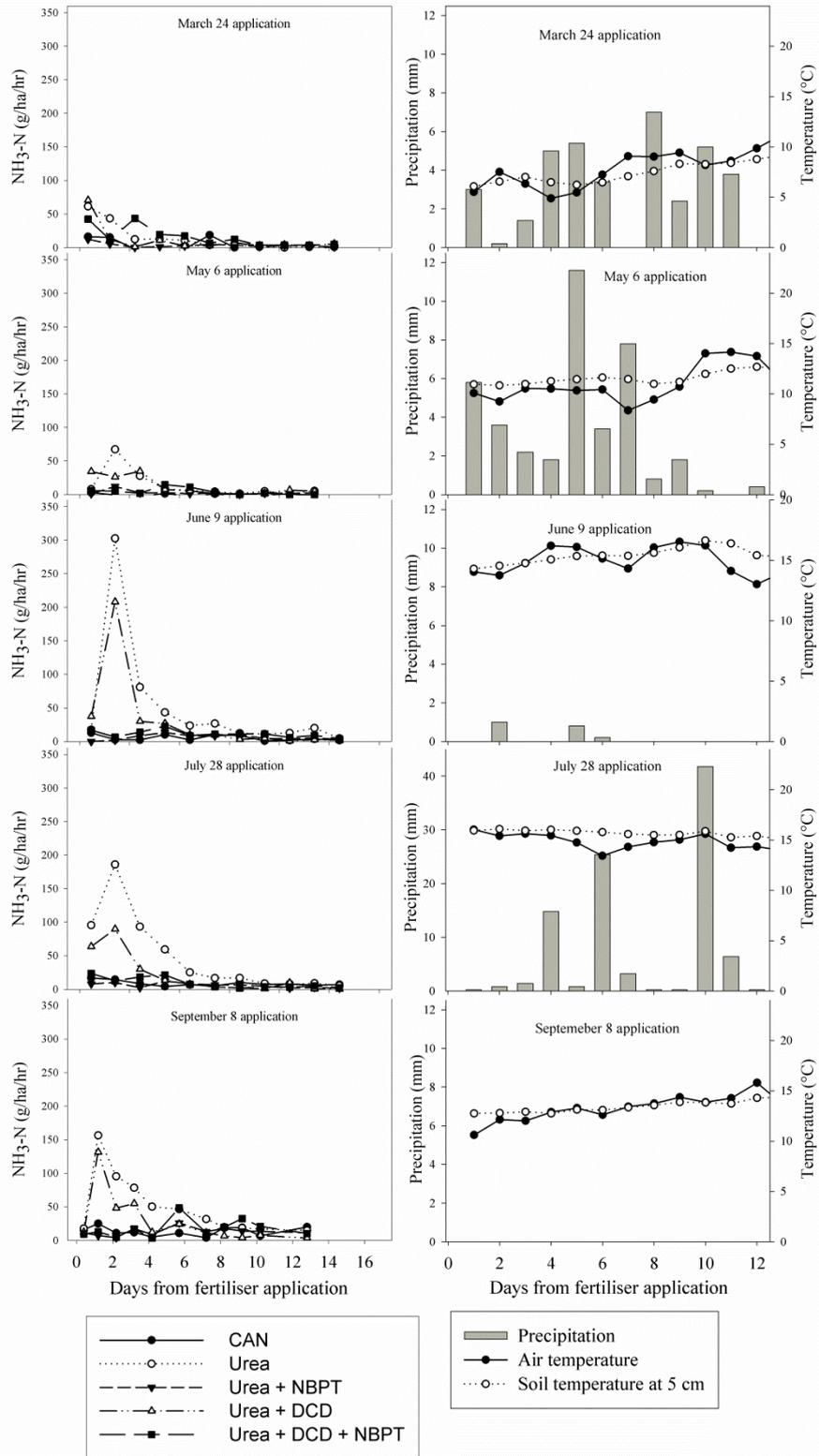
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478 **Figure captions**

479 Figure 1 Hourly ammonia (NH<sub>3</sub>) emissions by fertiliser N treatment, daily precipitation and  
480 mean daily air temperature for each fertiliser N application date at the Johnstown Castle site.



482 Figure 2 Hourly ammonia ( $\text{NH}_3$ ) emissions by fertiliser N treatment, daily precipitation and  
483 mean daily air temperature for each fertiliser N application date at the Hillsborough site.



486 Table 1 Ammonia loss as affected by fertiliser N treatment for each application date at the  
 487 Johnstown Castle and Hillsborough sites.

| Site   | Johnstown Castle                    |                  |  |          |           | Hillsborough |          |                     |           |           |      |
|--|-------------------------------------|------------------|--|----------|-----------|--------------|----------|---------------------|-----------|-----------|------|
| Season   | Spring                              |                  | Summer                                   |          |           | Spring       |          | Summer <sup>b</sup> |           |           |      |
| Fertiliser application date                            | Mar<br>10                           | Apr<br>28        | Jun<br>3                                 | Jul<br>7 | Aug<br>18 | Mar<br>24    | May<br>6 | Jun<br>9            | Jul<br>28 | Sept<br>8 |      |
| Volumetric moisture 0-5cm on day after application (%) | 45.4                                | 37.4             | 34.4                                     | 28.8     | 27.5      | 46           | 41.7     | 24.9                | 16.8      | 25.5      |      |
| Treatment  | N rate/<br>application<br>(kg N/ha) |                  | NH <sub>3</sub> -N loss (% of applied N) |          |           |              |          |                     |           |           |      |
| CAN  | 40                                  | 5 e <sup>a</sup> | 7 c                                      | 2 b      | 4 c       | 2 c          | 4 bc     | 2 b                 | 3 d       | 4 b       | 8 b  |
| Urea   | 40                                  | 53 c             | 25 b                                     | 20 a     | 26 a      | 30 b         | 21 a     | 8 b                 | 33 b      | 31 a      | 33 a |
| Urea   | 80                                  | 68 ab            | 38 ab                                    | 24 a     | 24 a      | 43 a         | 14 ab    | 19 a                | 49 a      | 34 a      | 43 a |
| Urea+NBPT  | 40                                  | 15 de            | 6 c                                      | 5 b      | 9 bc      | 6 c          | 2 c      | 2 b                 | 4 d       | 4 b       | 9 b  |
| Urea + DCD   | 40                                  | 77 a             | 42 a                                     | 22 a     | 22 a      | 45 a         | 9 bc     | 7 b                 | 20 c      | 13 b      | 19 b |
| Urea+NBPT+DCD  | 40                                  | 18 d             | 6 c                                      | 4 b      | 5 c       | 8 c          | 6 bc     | 2 b                 | 7 d       | 6 b       | 11 b |
| Urea+MIP   | 40                                  | 55 bc            | 34 ab                                    | 16 ab    | 21 ab     | 47 a         | -        | -                   | -         | -         | -    |

488 <sup>a</sup> Treatments with different letters within columns are different according to F-protected LSD test  
 489 ( $P<0.05$ ).

490 <sup>b</sup> for the purposes of seasonal comparison the conditions following the Sept 8 application were  
 491 considered close to those of summer and loss did not differ from summer at HB

492

493 Table 2 Annual ammonia loss as measured by wind tunnels and the change ( $\Delta$ ) in loss  
 494 compared with the urea 200 kg N/ha rate for the other treatments. N applied to grassland N  
 495 input in five equal split applications (40 or 80 kg N/ha).

| Site<br>Treatment | N rate<br>(kg/ha/yr) | JC<br>Total NH <sub>3</sub> -N loss<br>(% of applied) | HB<br>Total NH <sub>3</sub> -N loss<br>(% of applied) | JC<br>$\Delta$ NH <sub>3</sub> -N loss<br>(% $\Delta$ from urea 200<br>kg N/ha) | HB<br>$\Delta$ NH <sub>3</sub> -N loss<br>(% $\Delta$ from urea 200<br>kg N/ha) |
|-------------------|----------------------|---|---|---|---|
| C-A-N.            | 200                  | 4.1 d <sup>†</sup>                                    | 4.2 bc  | -87   | -83   |
| Urea              | 200                  | 30.6 c  | 25.1 a  |   |   |
| Urea              | 400                  | 40.0 ab   | 32.0 a  | 31  | 27  |
| Urea + NBPT       | 200                  | 8.2 d   | 4.0 c   | -73   | -84   |
| Urea + DCD        | 200                  | 41.6 a  | 13.7 b  | 36  | -45   |
| Urea + NBPT + DCD | 200                  | 8.1 d   | 6.5 bc  | -74   | -74   |
| Urea + MIP        | 200                  | 35.1 bc   | -   | 15 n.s.   | -   |

496 <sup>†</sup> Treatments with different letters within columns are different according to F-protected LSD test  
 497 ( $P < 0.05$ ).

498 n.s. not significant

499