Ammonia emissions from cattle dung, urine and urine with dicyandiamide in a temperate grassland

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Short running head title: NH_3 emissions from dung, urine and urine+DCD

Abstract

Deposition of urine and dung in pasture-based livestock production systems is a major source of ammonia (NH_3) volatilisation, contributing to the eutrophication and acidification of water bodies and to indirect nitrous oxide emissions. The objectives of this study were to (i) measure NH_3 volatilisation from dung and urine in three seasons, (ii) test the effect of spiking urine with the nitrification inhibitor dicyandiamide (DCD) on NH_3 volatilisation and (iii) generate NH_3 emission factors (EFs) for dung, urine and urine+DCD in temperate maritime grassland. Accordingly, simulated dung, urine and urine spiked with DCD (at 30 kg DCD/ha equivalent rate) patches were applied to temperate grassland. Treatments were applied three times in 2014 with one measurement of NH_3 loss being completed in spring, summer and autumn. The NH_3-N EF was highest in spring, which was most likely due to the near absence of rainfall throughout the duration of loss measurement. The EFs across the experiments ranged between 2.8 and 5.3 % (mean 3.9 %) for dung, 8.7 and 14.9 % (mean 11.2 %) for urine and 9.5 and 19.5 % (mean 12.9 %) for urine+DCD, showing that ammonia loss from dung was significantly lower than from urine. Aggregating country specific emission data such as those from the current experiment with data from climatically similar regions (perhaps in a weighted manner which accounts for the relative abundance of certain environmental conditions) along with modelling are potentially resource efficient approaches for refining national ammonia inventories.

Key words: Ammonia , dung, urine, DCD, grazing, grassland

Introduction

Livestock production systems are major contributors to global agricultural ammonia (NH_3) emissions and are responsible for between 16 and 27 (mean 21) Tg/yr emission. Grazing animals contribute between 17 and 37 % of this total (Beusen et al., 2008). Therefore, NH_3

emissions from livestock systems are a substantial issue in many countries, particularly in the European Union where member states have agreed to establish national NH_3 emission ceilings (European Commission, 2015). In Ireland, for example, agriculture contributes approximately 98 % of national NH_3 emissions and in 2012 it is estimated that 12 % of these emissions arose from dung and urine-N deposited by grazing livestock (EPA, 2014).

Ammonia volatilisation is a major loss pathway for nitrogen (N) from dung and urine deposited on pasture. Volatilisation represents a loss in terms of soil fertility and causes negative environmental impacts by contributing to eutrophication and acidification of water bodies (Grizzetti, 2011). In addition, NH_3 deposition results in acidification of soils due to release of H^+ during nitrification (Velthof, 2011). Ammonia is also vulnerable to the formation of secondary aerosols such as NH_4NO_3 and $(NH_4)_2SO_4$ because of its alkaline nature (Warneck, 1999). The transport distance of these secondary ammonium salt aerosols is considerably greater than for NH_3 gas (Warneck, 1999; Aneja et al., 2000). Furthermore, re-deposition of volatilised NH_3 is an important source of N for the production of nitrous oxide (N_2O) via biological nitrification of ammonium (NH_4^+) (Martikainen, 1985) and subsequent denitrification of nitrate (NO_3^-). Therefore, NH_3 contributes indirectly to greenhouse gas production. As a consequence, estimates of NH_3 emissions from urine and dung play an important role in determining the indirect element of N_2O emission factors (EFs) and are necessary to compliment recent studies which measured direct emission N_2O emissions from cattle excreta in temperate grassland (Bell et al., 2015; Krol et al,. 2015).

The rate of NH_3 volatilisation from dung and urine is influenced by meteorological factors such as temperature, rainfall and wind speed. Generally, weather conditions which increase evaporation will increase volatilisation of NH_3 (Meisinger & Jokela, 2000). Ammonia volatilisation increases with increasing temperature (Clay et al., 1990; Lockyer & Whitehead, 1990; Sommer et al., 1991; Whitehead & Raistrick, 1991) due to increased urease activity in

66 soil and decreased water solubility of NH_3 (Freney et al., 1983), provided adequate soil water
67 is present for hydrolysis of urea (Lockyer & Whitehead, 1990). The influence of rainfall on
68 emissions depends on the intensity of the rainfall event: small volumes of rainfall ($\leq$ 5 mm)
69 with low intensity increase NH_3 volatilisation due to enhanced hydrolysis of urea (Engel et
70 al., 2011; Sanz-Cobena et al., 2011), whereas higher volumes of rainfall minimise
71 volatilisation due to increased soil infiltration of deposited N (Bouwmeester et al., 1985;
72 Engel et al., 2011; Sanz-Cobena et al., 2011).
73 Mitigation strategies, such as the use of nitrification inhibitors, have been widely investigated
74 to assess their effectiveness in reducing N losses from urine patches. For example, the
75 nitrification inhibitor dicyandiamide (DCD) has been reported to reduce NO_3^- leaching losses
76 by 10 to 76 % (Di & Cameron, 2004; Zaman & Blennerhassett, 2010; Dennis et al., 2012)
77 and N_2O emissions from urine patches by 25 to 70 % (Di et al., 2007; Smith et al., 2008;
78 Zaman & Blennerhassett, 2010; Misselbrook et al., 2014). Dicyandiamide reduces these
79 losses by slowing the conversion of soil NH_4^+ to NO_3^- and consequently increases the period
80 of time in which soil NH_4^+ is available for NH_3 volatilisation. Therefore, although the use of
81 DCD is an effective leaching and N_2O emission mitigation strategy, it may promote increased
82 NH_3 volatilisation from urea fertilisers and urine patches. However, this has not been
83 consistently reported in the literature (Table 1): most previous studies (Prakasa Rao &
84 Puttanna, 1987; Davies & Williams, 1995; Asing et al., 2008; Zaman & Blennerhassett,
85 2010) have found increased NH_3 volatilisation in presence of DCD, whereas Clay et al.
86 (1990) and Di & Cameron (2004) did not observe a significant effect of DCD. Hence there is
87 some uncertainty as to the effect of DCD usage on NH_3 loss when used as a NO_3 and N_2O
88 loss mitigation strategy.
89 Table 1 here

At present, the grazing cattle contributions to national NH_3 inventories in many countries are estimates based on a limited number of urine and dung EF studies, often derived in other countries subject to differing environmental conditions. In Ireland's case, EFs from the UK are currently used. To address the urine and dung NH_3 emission knowledge gap for grazing systems in Ireland, the objectives of this study were to (i) measure NH_3 volatilisation from dung and urine across three seasons (spring, summer, autumn), (ii) test the effect of spiking urine with the nitrification inhibitor DCD on NH_3 volatilisation and (iii) generate NH_3 EFs for dung, urine and urine+DCD, all in grassland in temperate maritime climatic conditions using dung and urine collected from animals grazing in these individual seasons.

Material and Methods

Experimental Site and Experimental Design

The experiment was conducted at a grassland site located at Teagasc Research Centre, Johnstown Castle, Co. Wexford, Ireland (52˚18´N, 6˚30´W; 62 m above sea level). In this area of Ireland the mean annual air temperature is 10.6 °C and the mean annual precipitation is 905.5 mm (Met Éireann, 2015). The soil is a luvic gleysol with a loam texture at the surface (0 to 10 cm depth). Soil properties (0 to 10 cm depth) at the site are presented in Table 2. The sward was a perennial ryegrass (*Lolium perenne* L.) and white clover mixture (*Trifolium repens* L.).

Table 2 here

The experimental design was a randomised complete block with three treatments and three replicates per treatment. The treatments were (i) dung, (ii) urine and (iii) urine+DCD. These treatments were applied three times over the course of the experiment to represent dung and urine depositions in spring, summer and autumn.

Weather and Soil Conditions

Meteorological parameters including air temperature, air pressure, rainfall and wind speed were recorded on an hourly basis at the nearest automatic weather station "Johnstown Castle" from the Irish Meteorological Service (Met Éireann) (ca. 500 m distant from the study site). Additionally, volumetric soil moisture in field was determined weekly with a theta probe (Delta-T, Cambridge, UK).

Collection and Application of Dung and Urine

Dung and urine were collected 7 to 10 days before each application. Urine was collected directly from lactating Holstein-Friesian dairy cows by stimulating the cows' perineum before and after evening milking. The dung was collected in the field immediately following deposition. In all seasons, the cows' diet consisted of grazed perennial ryegrass pasture. Urine and dung were homogenised following collection and stored in sealed plastic containers at 4 °C until application to reduce the risk of NH_3 volatilisation. For the urine+DCD treatment, DCD was added at a rate to deliver equivalent of 30 kg DCD/ha on application. Luo et al. (2015) indicated that increasing the DCD application rate from 10 to 60 kg/ha could decrease N_2O emissions from urine patches; the DCD rate chosen in this study was the same as their mid-point rate of 30 kg/ha.

Treatment application took place on 8 April 2014, 28 July 2014 and 30 September 2014 for spring, summer and autumn applications, respectively. The dung patches were simulated by applying 2 kg of fresh dung, which is within the range of 1.5-2.7 kg reported by Haynes and Williams (1993), in a constrained 28 cm diameter ring (0.0615 m^2). Four of these dung patches were applied in a square configuration (edge length: 1 m), with the centre of the dung patch placed on each corner of the square. The urine and urine+DCD patches were applied in the same square configuration. These patches were simulated using 2 L of urine, the same

139 volume as used by Williams and Haynes (1994) and close to the 2.1 L mean urination volume
140 from dairy cows reported in a meta-analysis by Selbie et al. (2014), and were applied using a
141 watering can with a rosette attachment. The urine patches were constrained to a 0.16 m^2
142 surface area using a stainless steel frame which was placed in the ground to a maximum
143 depth of 1 cm and removed promptly following urine infiltration into the soil. The sward was
144 cut to a uniform height of 5 cm ten days before each of the three treatment applications and
145 allowed to regrow. A new plot was used for each of the three seasonal applications.
146
147 *Ammonia Emission Measurement*
148 A system of nine wind tunnels (Lockyer, 1984), were deployed to measure NH_3
149 volatilisation. Briefly, each wind tunnel unit consisted of (i) a canopy (0.5 m x 2 m) made of
150 polycarbonate into which an inlet air sample line was integrated, (ii) a galvanised sheet steel
151 duct housing an axial fan, anemometer and an outlet air sample line and (iii) a control box
152 housing a diaphragm pump for the air sample lines, a flow meter and a critical orifice for both
153 air sample lines. The air pumped through the inlet and outlet air sample lines passed through
154 two individual conical absorption flasks which contained 100 ml of 0.02 M orthophosphoric
155 acid (H_3PO_4, 85 %, Merck, Darmstadt, Germany), to capture NH_3-N in the air (i.e. acid
156 traps).
157 The wind tunnel canopy was placed over two of the four urine or dung patches on each
158 replicate immediately after treatment application. Emissions were measured continuously for
159 a period of 15 to 17 days after each application. The acid traps were replaced every ~24 h
160 (except during the first 24 h period in the summer application when they were changed twice
161 in the initial 24 h), until 10^{th} day after application and thereafter every ~48 h until the end of
162 the experiment. The rain-shielding effect of the wind tunnel canopy in periods of rain was

minimized by moving the canopy back and forth between the two pairs of simulated urine or dung patches on each occasion that the acid traps were changed.

To account for evaporation in the field the acid trap samples were refilled to 100 ml with deionised water (Sartorius arium 611UV, Göttingen, Germany), decanted in plastic tubes (50 ml, Sarstedt, Nürnbrecht, Germany), and stored at 4 °C until analysed.

Ammonium Analysis

The ammonium-N concentration in the acid trap samples (NH_4^+-N in 0.02 M H_3PO_4) was determined photometrically using an Aquakem 600A Analyser (Thermo Electron OY, Vantaa, Finland). Ammonium was converted by reaction with hypochlorite ions and salicylate ions into a blue compound. After 600 s incubation time absorbance was measured at wavelength 660 nm. The detection limit was 0.02 mg/L.

Dung and Urine Analysis

On each day of application, subsamples from the dung, urine and urine+DCD to be applied were taken and analysed for total N. A 10 mL portion of the urine subsamples was diluted 1:500 with deionised water (Sartorius arium 611UV, Göttingen, Germany) and then analysed unfiltered with Ganimede N (Hach-Lange, Düsseldorf, Germany). The dry matter content of dung samples was measured by freeze drying. A portion of the freeze-dried sample was ball milled and analysed for total N content with LECO TruSpec CN (St. Joseph, USA).

Data Analysis

The calculation of NH_3-N loss in kg/ha was carried out as described by Meisinger et al. (2001). If the difference between the inlet and outlet acid trap concentration was negative the loss was set to zero. The NH_3-N flux was calculated by dividing the emission rate by the

exposure time. The statistical analysis software R (version 3.1.2, R Development Core Team, 2014) was used to test for treatment effects with mean comparisons by F-protected LSD test. Data from each season were analysed separately because the effect of season was confounded with the effect of the slightly changed location at each application. A statistical probability of $P < 0.05$ was considered significant for all statistical tests.

Results

Weather Conditions

The average air temperatures during the measurement periods were 9.1, 15.4 and 11.6 °C during the spring, summer and autumn applications, respectively (Table 3). Total rainfall varied greatly between experimental periods (Table 3). During the spring application cumulative rainfall and intensity (Figure 1d) was very low compared with the summer and autumn applications (Figures 1i, n). Additionally, little rainfall occurred during the initial 11 days following the spring application (Figure 1d). The initial volumetric soil moisture at treatment application was highest in spring (42 %) and lowest in summer (11 %), while there was little difference in mean wind speed between seasons.

Table 3 here

Dung and Urine N Content, Dry Matter and N Loading

Dung dry matter contents were 15, 12 and 9 % for spring, summer and autumn applications, respectively. The dung N loading was highest in spring (Table 4). The mean urine N load was 695 kg/ha or in the case of urine+DCD 717 kg/ha (Table 4), with the highest N loading in summer.

Table 4 here

212 *Ammonia Emissions*

213 Hourly ammonia emissions (kg NH_3-N/ha/h) ranged from 0 to 0.66 kg N/ha/h for dung, 0 to
214 1.7 kg N/ha/h for urine and 0 to 2.02 kg N/ha/h for urine+DCD (Figures 1a, f, k). Hourly
215 emissions peaked within the first two days following application for urine treatments and
216 declined thereafter until the end of the measurement period in each season. Hourly NH_3
217 emissions from dung were lower compared to urine treatments in the first four days after each
218 application and displayed little temporal variation within each season.

219 Emissions from urine treatments were rapid following application, with the majority (> 80 %)
220 of the NH_3-N emissions occurring within the first three days in each of the three seasons
221 (Figures 1b, j, l). Emissions from dung followed a more consistent emission pattern with
222 > 80 % of the emissions occurring within 11 to 14 days of application in each of the three
223 seasons (Figures 1b, j, l).

224 Figure 1 here

225

226 Total NH_3-N losses and EFs for each season are presented in Table 5. The EFs for urine
227 treatments were significantly higher than the dung in each season. However, the EFs for urine
228 and urine+DCD did not differ significantly. Substantial differences in NH_3 loss, particularly
229 for urine and urine+DCD, were noted between spring and the other two seasons. These
230 differences were not statistically evaluated as the experiment was not randomised to
231 accommodate such comparison bearing in mind that the specific environmental factors
232 following dung and urine application were expected to have a large influence on the
233 measured EFs. Over the three applications dates the mean EFs were 3.9, 11.1, and 12.9 % for
234 dung, urine and urine+DCD, respectively.

235 Table 5 here

Discussion

Ammonia Emission Factors

The NH_3-N EFs for urine across the three seasons ranged between 8.7 % and 14.9 % (Table 5). Other researchers have observed larger ranges in urine EFs for temperate grassland. For instance, EFs for urine ranged between 3.7 % and 26.9 % in the UK (Ryden et al., 1987; Lockyer & Whitehead, 1990), between 3 % and 52 % in Denmark (Petersen et al., 1998) and between 3.6 % and 23 % in New Zealand (Zaman et al., 2009, 2013; Zaman & Blennerhassett, 2010). The lower range of emissions in the current experiment may be in part due to the small range in rainfall quantities experienced during the initial days following each urine application (Figure 1d, i, n). Ammonia EFs for urine applied to grassland have been found to decrease four-fold with the application of simulated rainfall (20 mm) immediately after urine application, compared to urine receiving no rainfall (Saarijärvi *et al.*, 2006). This is a period which is highly influential on cumulative NH_3 loss as illustrated by Lockyer and Whitehead (1990) who reported that at least 70% of NH_3 loss occurred within four days of urine application and the current experiments where >80% of emissions occurred within three days of urine application.

In the current experiments, dung NH_3-N EFs ranged between 2.8 % and 5.3 % (Table 5). These values are consistent with values reported in the literature for dung EFs from temperate grassland of 1.2 % (Ryden et al., 1987), 4.7 % (MacDiarmid & Watkin, 1972) but substantially lower than the 11.6 % reported by Laubach et al. (2013); Petersen et al. (1998) detected only "insignificant" NH_3 volatilisation from dung pats. The lower NH_3 emission from dung compared to urine in this and previous studies is most likely due to the form of N in dung which is bound in proteins and bacterial cells as compared to the high proportion of urea N present in urine (Ryden et al., 1987). Petersen et al. (1998) suggested that the lower

emission from dung could also be due to the formation of a surface crust on the dung pat which limits NH_3 volatilisation.

The somewhat lower EFs reported in this study may be due, in part, to the specific environmental conditions experienced at the experimental site following the treatment applications. Inconsistency in EFs between studies conducted in different countries and indeed within countries is to be expected. This is because measurements are taken from a subsample of all possible soil and environmental conditions which occur in a given country and ammonia loss is heavily influenced by these factors. This presents challenges for generating robust loss estimates for grazing systems were urine and dung are deposited continually during the grazing season and each patch is subject to a very specific set of soil and environmental conditions flowing deposition. The generation of country-specific EFs is important to help refine the accuracy of national NH_3 emissions inventories, but importantly so too is the generation of larger NH_3 loss datasets across countries with similar climatic conditions. Given the limitations of subsampling all possible climatic and soil conditions which a urine or dung patch will be subjected to in a specific country, a practical approach may be to aggregate studies which have assessed loss under environmental conditions which are representative of a country. It may be useful to do this in weighted manner which takes account of the relative occurrence of the environmental conditions of specific experiments. This approach has potential to generate a more robust climatic (rather than country specific) EF. Currently emissions from dung and urine for Irelands' national NH_3 emissions inventory are estimated using UK data, these loss estimates can be improved by incorporation of country specific data such those from the current study.

Temporal variation in NH_3 loss

The temporal pattern of NH_3 emission peaks for urine treatments was similar between seasons (Figures 1a, b, f, g, k, l). However, the emission period was substantially longer in spring than in summer and autumn experiments (14 days versus eight and seven days, respectively). Accordingly, higher cumulative emissions were measured in spring. In general, emissions in spring are thought to be lower than in summer and autumn due, in part, to lower air temperatures. Several studies have found NH_3 volatilisation to increase with increasing air temperature (Clay et al., 1990; Lockyer & Whitehead, 1990; Sommer et al., 1991; Whitehead & Raistrick, 1991). However, the highest emission in this experiment was measured in spring which had the lowest air temperature (Table 3). This highlights the point that other factors can play an influence which overrides the temperature effect on NH_3 loss. The high spring emissions observed can be explained by both high emission on day two and the protracted period of NH_3 emission in the spring measurement where rainfall did not occur (Figure 1d). The lack of rainfall may have allowed for this protracted period of NH_3 loss compared to other seasons. Previous studies have reported that significant levels of rainfall/irrigation, soon after application, can restrict NH_3 emissions from urea fertiliser (Bouwmeester et al., 1985; Engel et al., 2011; Sanz-Cobena et al., 2011) and urine patches (Saarijärvi *et al.*, 2006).

Initial soil moisture content was highest in spring (Table 3) which may have promoted NH_3 loss due to increased urease activity (McGarry et al., 1987; Kemppainen, 1989; Whitehead & Raistrick, 1991). Higher initial soil moisture contents may have slowed the infiltration of urine N into the soil profile, contributing to the large peak in NH_3 loss observed in spring (Figure 1a). Similarly, Sommer & Jacobsen (1999) reported lower infiltration of slurry ammoniacal N and increased NH_3 volatilisation. Furthermore, protracted drying conditions due to the absence of rainfall (Figure 1d) for most of the duration of measurement in spring is consistent with higher NH_3 loss due to a prolonged emission period in addition to the initial

peak (Figure 1a). In the absence of rainfall, previous studies (Burch & Fox, 1989; Engel et al., 2011) have reported greater NH_3 volatilisation from urea fertiliser which could be either due to an increased transition of dissolved to gaseous NH_3 which is lost to the atmosphere or due to increased soil water evaporation and subsequent volatilisation of NH_3 dissolved in soil water.

Impact of Dicyandiamide on Ammonia Emissions

Although there is strong evidence in the literature, summarised by Kim et al. (2012), that the use of a nitrification inhibitor can increase NH_3 emissions, there was no statistical difference between urine and urine+DCD in the current experiments. However, in two seasons a trend towards increased EFs was present. Although not significantly different, EFs for the urine+DCD treatments in spring and autumn were numerically 31 % ($P = 0.2$) and 9 % ($P = 0.38$) higher compared to urine only. The soil properties at this site may have contributed to the lack of difference in NH_3 emissions between urine and urine+DCD treatments. For instance, a meta-analysis conducted by Kim et al. (2012) found that studies in which DCD significantly increased NH_3 volatilisation relative to control treatments (e.g. Davies & Williams,1995; Asing et al., 2008; Table 1) had an average soil pH of 6.5 and CEC of 10.2 meq/(100 g), whereas the soils in studies with no significant effect of DCD (e.g. Di & Cameron, 2004; Table 1) had lower soil pH (5.5) and higher CEC (15.8 meq/(100 g)). These lower pH and higher CEC values are similar to the soil pH and CEC in the present study (5.8 and 15.5 meq/(100 g), Table 2). Therefore, the pH and high CEC of the soil at this site may have mitigated against DCD increasing NH_3 volatilisation loss.

Conclusions

Mean ammonia EFs in this study were 3.9 (2.8–5.3 %), 11.1 (8.7–14.9 %) and 12.9 % (9.5–19.5 %) for dung, urine and urine+DCD, respectively. Differing EFs between seasons were

attributed to the contrasting soil and ambient environmental conditions immediately following application of dung and urine, specifically soil moisture, and precipitation volume and pattern following application. The results of this experiment will aid refinement of national NH_3 inventories in Ireland and add to the limited body of excreta EFs available for temperate maritime grassland, particularly for urine+DCD. Other researchers have shown increased NH_3 emissions when nitrification inhibitors are used. However, the current experiments did not detect such an effect, indicating that increased NH_3 loss due to nitrification inhibitor usage will not occur in all cases. The present study highlights the need to fully understand the potential pollution swapping implications of utilising nitrification inhibitors as an N_2O loss mitigation strategy because their effect on NH_3 loss remains difficult to predict. Further research is needed to identify techniques for NH_3 mitigation from dung and urine, and practical and cost-effective mechanisms for implementation in grazing systems, which is quite challenging owing to the spatially and temporally haphazard nature of excreta deposited at pasture.

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References

Aneja, V.P., Chauhan, J.P., & Walker, J.T. 2000. Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. *Journal of Geophysical Research: Atmospheres* **105**, 11535–11545.

358 Asing, J., Saggar, S., Singh, J., & Bolan, N.S. 2008. Assessment of nitrogen losses from urea
359 and an organic manure with and without nitrification inhibitor, dicyandiamide,
360 applied to lettuce under glasshouse conditions. *Australian Journal of Soil Research*
361 **46**, 535–541.

362 Bell, M.J., Rees, R.M., Cloy, J.M., Topp, C.F.E., Bagnall, A., & Chadwick, D.R. 2015.
363 Nitrous oxide emissions from cattle excreta applied to a Scottish grassland: Effects of
364 soil and climatic conditions and a nitrification inhibitor. *Science of the Total*
365 *Environment* **508,** 343-353.

366 Beusen, A.H.W., Bouwman, A.F., Heuberger, P.S.C., Van Drecht, G., & Van Der Hoek,
367 K.W. 2008. Bottom-up uncertainty estimates of global ammonia emissions from
368 global agricultural production systems. *Atmospheric Environment* **42**, 6067–6077.

369 Bouwmeester, R.J.B., Vlek, P.L.G., & Stumpe, J.M. 1985. Effect of environmental factors on
370 ammonia volatilization from a urea-fertilized soil. *Soil Science Society of America*
371 *Journal* **49**, 376–381.

372 Burch, J.A., & Fox, R.H. 1989. The effect of temperature and initial soil moisture content on
373 the volatilization of ammonia from surface-applied urea. *Soil Science* **147**, 311–318.

374 Clay, D.E., Malzer, G.L., & Anderson, J.L. 1990. Ammonia volatilization from urea as
375 influenced by soil temperature, soil water content, and nitrification and hydrolysis
376 inhibitors. *Soil Science Society of America Journal* **54**, 263–266.

377 Davies, D.M., & Williams, P.J. 1995. The effect of the nitrification inhibitor dicyandiamide
378 on nitrate leaching and ammonia volatilization: A UK nitrate sensitive areas
379 perspective. *Journal of Environmental Management* **45**, 263–272.

380 Dennis, S.J., Cameron, K.C., Di, H.J., Moir, J.L., Staples, V., Sills, P., & Richards, K.G.
381 2012. Reducing nitrate losses from simulated grazing on grassland lysimeters in
382 Ireland using a nitrification inhibitor (Dicyandiamide). p. 1–11. *In* Biology &
383 Environment: Proceedings of the Royal Irish Academy.

384 Di, H.J., & Cameron, K.C. 2004. Treating grazed pasture soil with a nitrification inhibitor,
385 eco-n^{TM}, to decrease nitrate leaching in a deep sandy soil under spray irrigation—a
386 lysimeter study. *New Zealand Journal of Agricultural Research* **47**, 351–361.

387 Di, H.J., Cameron, K.C., & Sherlock, R.R. 2007. Comparison of the effectiveness of a
388 nitrification inhibitor, dicyandiamide, in reducing nitrous oxide emissions in four
389 different soils under different climatic and management conditions. *Soil Use and*
390 *Management* **23**, 1–9.

391 Engel, R., Jones, C., & Wallander, R. 2011. Ammonia Volatilization from Urea and
392 Mitigation by NBPT following Surface Application to Cold Soils. *Soil Science*
393 *Society of America Journal* **75**, 2348–2357.

394 EPA. 2014. Informative Inventory Report 2014 – Air pollutant emissions in Ireland 1990–
395 2012 reported to the secretariat of the UNECE convention on long-range
396 transboundary air pollution. Environmental Protection Agency, Johnstown Castle.

European Commission. 2015. National Emission Ceilings. Available at http://ec.europa.eu/environment/air/pollutants/ceilings.htm (verified 18 March 2015).

Freney, J.R., Simpson, J.R., & Denmead, O.T. 1983. Volatilization of Ammonia. p. 1–32. *In* Simpson, J.R., Freney, J.R. (eds.), Gaseous Loss of Nitrogen from Plant-Soil Systems. Developments in Plant and Soil Sciences. Springer.

Grizzetti, B. 2011. Nitrogen as a threat to European water quality. p. 379–404. *In* Sutton, M.A., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B. (eds.), The European Nitrogen Assessment: Sources, Effects and Policy Perspectives. Cambridge University Press, Cambridge and New York.

Haynes, R.J., & Williams, P.H., 1993. Nutrient cycling and soil fertility in the grazed pasture ecosystem. *Advances in Agronomy* **49**, 119-199.

Kemppainen, E. 1989. Nutrient content and fertilizer value of livestock manure with special reference to cow manure. *Annales Agriculturae Fenniae* **28**, 163–284.

Kim, D.-G., Saggar, S., & Roudier, P. 2012. The effect of nitrification inhibitors on soil ammonia emissions in nitrogen managed soils: a meta-analysis. *Nutrient Cycling in Agroecosystems* **93**, 51–64.

Krol, D.J., Forrestal, P.J., Lanigan, G.J., and Richards, K.G. 2015. In situ N_2O emissions are not mitigated by hippuric and benzoic acids under denitrifying conditions. *Science of the Total Environment* **511** 352-358.

Laubach, J., Taghizadeh-Toosi, A., Gibbs, S.J., Sherlock, R.R., Kelliher, F.M., & Grover, S.P.P. 2013. Ammonia emissions from cattle urine and dung excreted on pasture. *Biogeosciences* **10**, 327–338.

Lockyer, D.R. 1984. A system for the measurement in the field of losses of ammonia through volatilisation. *Journal of the Science of Food and Agriculture* **35**, 837–848.

Lockyer, D.R., & Whitehead, D.C. 1990. Volatilization of ammonia from cattle urine applied to grassland. *Soil Biology and Biochemistry* **22**, 1137–1142.

Luo, J., Ledgard, S., Wise, B., Welten, B., Lindsey, S. Judge, A., & Sprosen, M. Effect of dicyandiamide (DCD) delivery method, application rate, and season on pasture urine patch nitrous oxide emissions. *Biology and Fertile Soils* **51**, 453-464.

MacDiarmid, B.N., & Watkin, B.R. 1972. The cattle dung patch. 2. Effect of a dung patch on the chemical status of the soil, and ammonia nitrogen losses from the patch. *Grass and Forage Science* **27**, 43–47.

Martikainen, P.J. 1985. Nitrous oxide emission associated with autotrophic ammonium oxidation in acid coniferous forest soil. *Applied and Environmental Microbiology* **50**, 1519–1525.

McGarry, S.J., O'Toole, P., & Morgan, M.A. 1987. Effects of soil temperature and moisture content on ammonia volatilization from urea-treated pasture and tillage soils. *Irish Journal of Agricultural Research*, 173–182.

435 Meisinger, J.J., & Jokela, W.E. 2000. Ammonia volatilization from dairy and poultry manure.
436 *Managing Nutrients and Pathogens from Animal Agriculture (NRAES-130)*, 334–354.

437 Meisinger, J.J., Lefcourt, A.M., & Thompson, R.B. 2001. Construction and Validation of
438 Small Mobile Wind Tunnels for Studying Ammonia Volatilization. *Applied*
439 *Engineering in Agriculture* **17**, 375–384.

440 Met Éireann. 2015. Average Weather in Rosslare 1978–2007. Available at
441 http://www.met.ie/climate-ireland/1981-2010/rosslare.html (verified 23 January
442 2015).

443 Misselbrook, T.H., Cardenas, L.M., Camp, V., Thorman, R.E., Williams, J.R., Rollett, A.J.,
444 & Chambers, B.J. 2014. An assessment of nitrification inhibitors to reduce nitrous
445 oxide emissions from UK agriculture. *Environmental Research Letters* **9**, 115006.

446 Petersen, S.O., Sommer, S.G., Aaes, O., & Søegaard, K. 1998. Ammonia losses from urine
447 and dung of grazing cattle: effect of N intake. *Atmospheric Environment* **32**, 295–300.

448 Prakasa Rao, E.V.S., & Puttanna, K. 1987. Nitrification and ammonia volatilisation losses
449 from urea and dicyandiamide-treated urea in a sandy loam soil. *Plant and Soil* **97**,
450 201–206.

451 R Development Core Team. 2014. R: A language and environment for statistical computing.
452 R Foundation for Statistical Computing, Vienna.

453 Rodgers, G.A. 1983. Effect of dicyandiamide on ammonia volatilisation from urea in soil.
454 *Fertilizer Research* **4**, 361–367.

455 Ryden, J.C., Whitehead, D.C., Lockyer, D.R., Thompson, R.B., Skinner, J.H., & Garwood,
456 E.A. 1987. Ammonia emission from grassland and livestock production systems in
457 the UK. *Environmental Pollution* **48**, 173–184.

458 Saarijärvi, K., Mattila, P.K., & Virkajärvi, P. 2006. Ammonia volatilization from artificial
459 dung and urine patches measured by the equilibrium concentration technique (JTI
460 method). *Atmospheric Environment* **40**, 5137-5145.

461 Sanz-Cobena, A., Misselbrook, T., Camp, V., & Vallejo, A. 2011. Effect of water addition
462 and the urease inhibitor NBPT on the abatement of ammonia emission from surface
463 applied urea. *Atmospheric Environment* **45**, 1517–1524.Selbie, D.R., Buckthought,
464 L.E., and Shepherd, M.A., 2014. The challenge of the urine patch for managing
465 nitrogen in grazed pasture systems. *Advances in Agronomy*, vol. 129: 229-292.

466 Smith, L.C., deKlein, C.A.M., & Catto, W.D. 2008. Effect of dicyandiamide applied in a
467 granular form on nitrous oxide emissions from a grazed dairy pasture in Southland,
468 New Zealand. *New Zealand Journal of Agricultural Research* **51**, 387–396.

469 Sommer, S.G., Hansen, M.N., & Søgaard, H.T. 2004. Infiltration of Slurry and Ammonia
470 Volatilisation. *Biosystems Engineering* **88**, 359–367.

471 Sommer, S.G., & Jacobsen, O.H. 1999. Infiltration of slurry liquid and volatilization of
472 ammonia from surface applied pig slurry as affected by soil water content. *The*
473 *Journal of Agricultural Science* **132**, 297–303.

474 Sommer, S.G., Jensen, L.S., Clausen, S.B., & SøGaard, H.T. 2006. Ammonia volatilization
475 from surface-applied livestock slurry as affected by slurry composition and slurry
476 infiltration depth. *The Journal of Agricultural Science* **144**, 229–235.

477 Sommer, S.G., Olesen, J.E., & Christensen, B.T. 1991. Effects of temperature, wind speed
478 and air humidity on ammonia volatilization from surface applied cattle slurry. *The*
479 *Journal of Agricultural Science* **117**, 91–100.

480 Velthof, G. 2011. Nitrogen as a threat to European soil quality. p. 495–510. *In* Sutton, M.A.,
481 Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B.
482 (eds.), The European Nitrogen Assessment: Sources, Effects and Policy Perspectives.
483 Cambridge University Press, Cambridge and New York.

484 Warneck, P. 1999. Chemistry of the Natural Atmosphere. 2nd ed. Academic Press, San
485 Diego.

486 Williams, P.H., & Haynes, R.J. 1994. Comparison of initial wetting pattern, nutrient
487 concentrations in soil solution and fate of ^{15}N-labelled urine in sheep and cattle urine
488 patch areas of pasture soil. *Plant and Soil* **162**: 49-59.

489 Whitehead, D.C., & Raistrick, N. 1991. Effects of some environmental factors on ammonia
490 volatilization from simulated livestock urine applied to soil. *Biology and Fertility of*
491 *Soils* **11**, 279–284.

492 Zaman, M., & Blennerhassett, J.D. 2010. Effects of the different rates of urease and
493 nitrification inhibitors on gaseous emissions of ammonia and nitrous oxide, nitrate
494 leaching and pasture production from urine patches in an intensive grazed pasture
495 system. *Agriculture, Ecosystems & Environment* **136**, 236–246.

496 Zaman, M., & Nguyen, M.L. 2012. How application timings of urease and nitrification
497 inhibitors affect N losses from urine patches in pastoral system. *Agriculture,*
498 *Ecosystems & Environment* **156**, 37–48.

499 Zaman, M., Saggar, S., Blennerhassett, J.D., & Singh, J. 2009. Effect of urease and
500 nitrification inhibitors on N transformation, gaseous emissions of ammonia and
501 nitrous oxide, pasture yield and N uptake in grazed pasture system. *Soil Biology and*
502 *Biochemistry* **41**, 1270–1280.

503 Zaman, M., Zaman, S., Nguyen, M.L., Smith, T.J., & Nawaz, S. 2013. The effect of urease
504 and nitrification inhibitors on ammonia and nitrous oxide emissions from simulated
505 urine patches in pastoral system: A two-year study. *Science of the Total Environment*
506 **465**, 97–106.

Table Captions

Table 1 Summary of literature reported influence of DCD on NH_3 volatilisation.

Table 2 Soil properties (0–10 cm depth) at the experimental site.

Table 3 Applied N rate for each season and treatment.

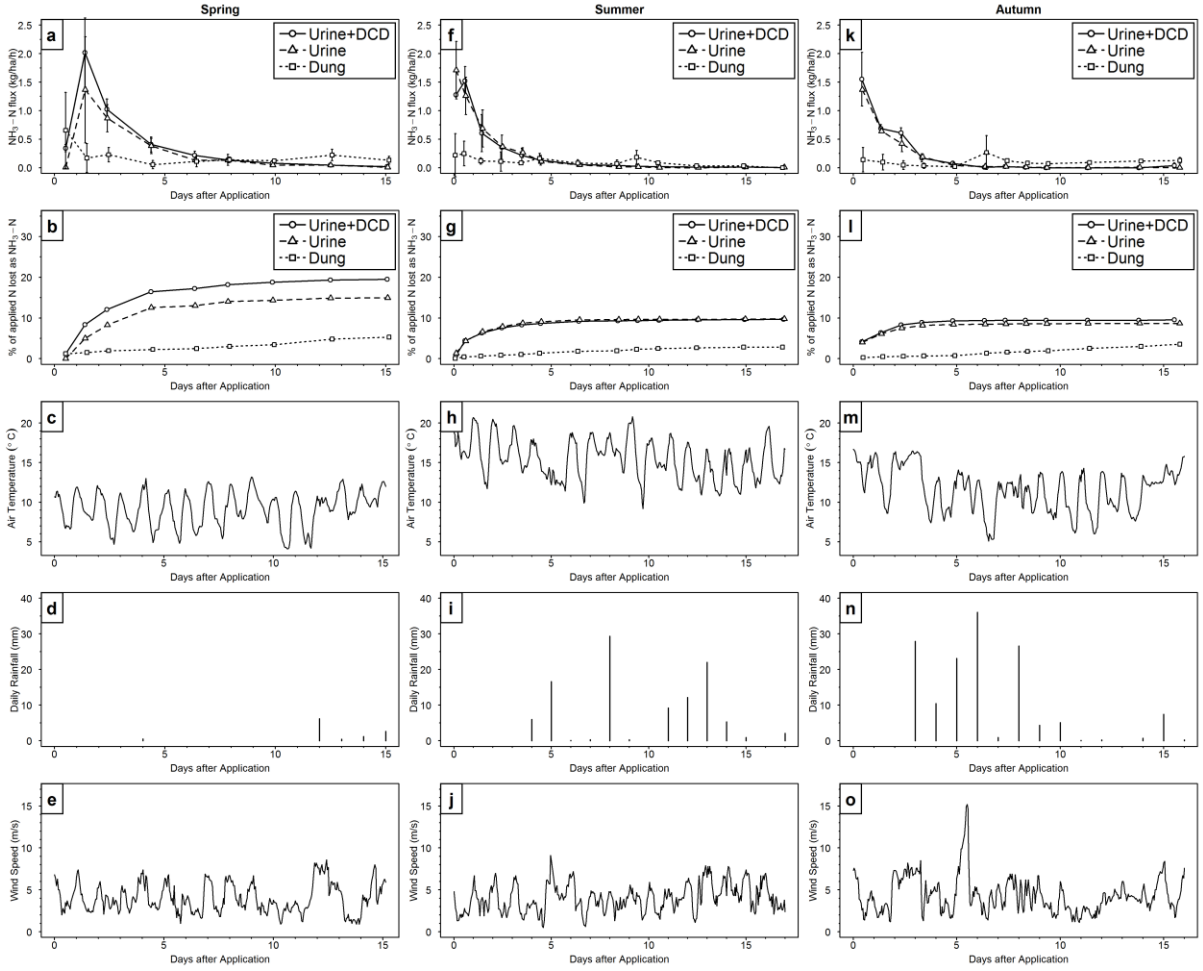
Table 4 Summary of weather conditions during each experimental period.

Table 5 Total NH_3-N losses and emission factors for spring, summer and autumn dung and urine applications.

514 **Figure Captions**

515

516 **Figure 1** Temporal trend of NH_3-N emissions and cumulative NH_3-N loss for dung, urine and
517 urine+DCD in spring, summer and autumn. Air temperature, daily rainfall and wind speed for
518 each experimental period. Error bars indicate standard deviation (n = 3).



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520

521 **Table 1**

Type of Study	Control	Treatment	Effect of DCD	Reference
Glasshouse	Urea, organic manure	Urea+DCD, organic manure+DCD	Increased volatilisation by 58 %* and 38 %	Asing et al. (2008)
Field	Urea	Urea+DCD	No effect	Clay et al. (1990)
Lysimeter	N-fertiliser	N-fertiliser+DCD	Significantly increased volatilisation	Davies & Williams (1995)
Lysimeter	Urea, urine	Urea+DCD, urine+DCD	No effect	Di & Cameron (2004)
Field	Urea	Urea+DCD	"Tremendous" increase in volatilisation	Prakasa Rao & Puttanna (1987)
Incubation	Urea	Urea+DCD	In- and decreased volatilisation	Rodgers (1983)
Lysimeter	Urine	Urine+DCD	Increased volatilisation by 41 %* and 18 %*	Zaman & Blennerhassett (2010)
Field	Urine	Urine+DCD	Increased volatilisation by 19 % and 55 %*	Zaman & Nguyen (2012)
Field	Urine	Urine+DCD	Increased volatilisation by 9–56 %	Zaman et al. (2009)
Field	Urine	Urine+DCD	Increased volatilisation by 10–45 %*	Zaman et al. (2013)

522 * Increase was significant

523

524 **Table 2**

Soil pH	CEC[a] (meq /(100 g))	Soil LOI[b] (%)	Soil Ca (mg/L)	Soil K (mg/L)	Soil Mg (mg/L)	Sand (%)	Silt (%)	Clay (%)
5.8	15.5	7.0	917	125	121	51.7	33.9	14.4

525 [a] Cation exchange capacity

526 [b] Loss on ignition

527

528 **Table 3**

	Spring	Summer	Autumn
Pressure (hPa)	1012	1002	999
Mean air temperature (°C)	9.1	15.4	11.6
Cumulative rainfall (mm)	10.9	104.2	142.9
Rain days	5	12	13
Initial volumetric soil moisture (%)	42	11	18
Mean wind speed (m/s)	4.0	4.0	4.4

529

530

Table 4

	Spring	Summer	Autumn
		kg N/ha	
Dung	1274 ± 263 †	1220 ± 83	1091 ± 47
Urine	638 ± 12	731 ± 6	716 ± 4
Urine+DCD	664 ± 8	746 ± 4	741 ± 4

† standard deviation

534 **Table 5**

	Total NH_3-N losses (kg/ha)			NH_3-N Emission factors (%)		
	Spring	Summer	Autumn	Spring	Summer	Autumn
Dung	67 ± 36[†]	34 ± 18	39 ± 12	5.3 b ‡	2.8 b	3.5 b
Urine	95 ± 19	72 ± 19	62 ± 7	14.9 a	9.8 a	8.7 a
Urine+DCD	129 ± 33	72 ± 25	71 ± 14	19.5 a	9.7 a	9.5 a

535 [†] standard deviation

536 [‡] Emission factors in the same column followed by a different letters are significantly
537 different according to the LSD test ($P < 0.05$).

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539