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Improving and disaggregating N_2O emission factors for ruminant excreta on temperate pasture soils

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Abstract

Cattle excreta deposited on grazed grasslands are a major source of the greenhouse gas (GHG) nitrous oxide (N_2O). Currently, many countries use the IPCC default emission factor (EF) of 2% to estimate excreta-derived N_2O emissions. However, emissions can vary greatly depending on the type of excreta (dung or urine), soil type and timing of application. Therefore three experiments were conducted to quantify excreta-derived N_2O emissions and their associated EFs, and to assess the effect of soil type, season of application and type of excreta on the magnitude of losses. Cattle dung, urine and artificial urine treatments were applied in spring, summer and autumn to three temperate grassland sites with varying soil and weather conditions. Nitrous oxide emissions were measured from the three experiments over 12 months to generate annual N_2O emission factors. The EFs from urine treated soil was greater (0.30 – 4.81% for real urine and 0.13 – 3.82% for synthetic urine) when compared with dung (-0.02 – 1.48%) treatments. Nitrous oxide emissions were driven by environmental conditions and could be predicted by rainfall and temperature before, and soil moisture deficit after application; highlighting the potential for a decision support tool to reduce

N_2O emissions by modifying grazing management based on these parameters. Emission factors varied seasonally with the highest EFs in autumn and were also dependent on soil type, with the lowest EFs observed from well-drained and the highest from imperfectly drained soil. The EFs averaged 0.31 and 1.18% for cattle dung and urine, respectively, both of which were considerably lower than the IPCC default value of 2%. These results support both lowering and disaggregating EFs by excreta type.

Key words: nitrous oxide; emission factor; grazed pasture; cattle excreta; dung; urine;

1. Introduction

Cattle excreta deposited on grazed grasslands is a major source of direct and indirect emissions of the greenhouse gas (GHG) nitrous oxide (N_2O), which has a global warming potential 298 times greater than CO_2 over a 100 year time horizon (IPCC, 2013). Transformations of N_2O in the stratosphere also lead to the destruction of the ozone layer (Ravishankara et al., 2009). Agriculture contributes to over 40% of global N_2O emissions (Denman et al., 2007), with managed grazed grasslands producing higher N_2O emissions compared with either un-grazed grasslands or arable cropland (van Groenigen et al., 2005). Grasslands occupy 25% of the earth's surface and provide feed for an estimated 1800 million livestock units (Saggar et al., 2009). However, due to low nitrogen (N) utilisation efficiency, 70-95% of N ingested by ruminant livestock is returned onto pasture as dung and urine (Oenema et al., 2005; Saggar et al., 2013). Emissions of N_2O arising from these returns comprise over 40% of the N_2O associated with animal production systems (Oenema et al., 2005). Therefore, N intake is a principal driver of N losses from ruminant livestock returns (Dijkstra et al., 2013).

77 Agriculture is the single largest contributor to Ireland's national GHG profile, producing 32% of
78 overall emissions (22.5 Mt CO_2—eq yr^{-1}; CSO, 2014; EPA, 2014). As the predominant agricultural
79 system is pastoral-based ruminant livestock production (Breen et al., 2010), grazing related N_2O
80 emissions have a proportionately large impact on sectoral emissions. Indeed, 90% of agricultural
81 land is devoted to improved grassland, or rough grazing, and supports 6.2 million cattle, including
82 1.3 million dairy cows (CSO, 2014; Duffy et al., 2014). However, there are large uncertainties around
83 the currently used estimate of 8.46 kt N_2O for urine and dung returned onto pasture, range, and
84 paddock (PRP) systems by grazing animals (Duffy et al., 2014). The current approach for quantifying
85 and reporting national N_2O emissions from PRP grazing returns is to use the default Tier 1 emission
86 factor (EF_{PRP}) of 2% from the current Intergovernmental Panel on Climate Change (IPCC) guidelines
87 (IPCC, 2006). This single EF_{PRP} is based upon a limited number of studies, some of them laboratory
88 based, and may not necessarily reflect country-specific conditions (Bell et al., 2015). The reported
89 EFs from urinary N vary widely, between 0.3 % (van der Weerden et al., 2011) and 13.3% (Kool et al.,
90 2006a). Additionally, the default EF_{PRP} does not take into account soil type, climatic conditions,
91 timing of deposition, or excreta form, all of which can influence the magnitude and duration of N_2O
92 emissions. Furthermore, the IPCC encourages the development of country-specific (Tier 2) factors,
93 especially for key N emission sources (de Klein et al., 2003). New Zealand developed and adopted a
94 country-specific EF_{PRP} over a decade ago (de Klein et al., 2003), later disaggregated by animal excreta
95 type, and the same process is currently underway in the UK, supported by the recently published
96 work of Bell et al. (2015) who produced the disaggregated EFs for Scottish grassland.
97 The main drivers of N_2O production in soils are mineral N content, soil water-filled pore space
98 (WFPS), and temperature (Conen et al., 2000). As a direct result of grazing returns, patches with very
99 high rates of N loading between 600 and 1000 kg N ha^{-1} are created (Welten et al., 2013; Selbie et
100 al., 2014). Between 50 and 90% of this excreted urinary-N is in the form of urea (Doak, 1952; Bristow
101 et al., 1992), which undergoes a rapid transformation to mineral N in soil. Nitrogen supply in excreta
102 patches exceeds the potential for assimilation and retention by plants, microorganisms and soil.

Therefore excess N is lost from the system through leaching of nitrate (NO_3^--N) and gaseous emissions (e.g. N_2O) (Saggar et al., 2011). In conditions where the N substrate is not a limiting factor, N_2O production is primarily affected by soil WFPS (Linn and Doran, 1984; van der Weerden et al., 2011; ME, 2015). North-West Europe has a temperate, humid climate with high rainfall in autumn and winter, leading to high soil WFPS, which could potentially result in higher denitrification rates and subsequent N_2O emissions from excreta deposited onto pasture at those times of year (Bell et al., 2015). Denitrification rates in Irish pasture soils have also been shown to be highly sensitive to temperature (Abdalla et al., 2009).

A rise in ruminant numbers and associated GHG emissions is anticipated as a consequence of both a rising demand for meat and dairy produce and the recent removal of EU milk quotas. Therefore accurate accounting and reporting of national N_2O emissions stemming from excreta, as well as mitigation strategies, are urgently needed (Oenema et al., 2005). Existing and anticipated mitigation options include improved soil and fertiliser management (such as the addition of nitrification inhibitors), effluent management, reducing wet season grazing and animal interventions, such as altered diet, feed additives and selective animal breeding (de Klein and Eckard, 2008; Luo et al, 2010). However, in order to plan and implement suitable N_2O mitigation strategies, a better handle on quantifying emissions and identifying the processes responsible for N_2O production is of paramount importance (Bell et al., 2015).

The aim of this work was to reduce the uncertainty around the quantity of N_2O emitted from agricultural animal excreta deposited onto pasture. Specific objectives of the study were to: 1) investigate the timing of cattle dung and cattle urine deposition and soil type on N_2O emissions from temperate pasture, range, and paddock; and 2) to elucidate the drivers of N_2O emissions from dung and urine returns to temperate pasture, range, and paddock.

2. Materials and Methods

129 2.1 Soil and site description and experimental design

130 The experiment was carried out across three seasons, at three experimental field sites on
131 contrasting soils across Ireland. The soils were a well drained sandy loam located at Teagasc
132 Moorepark, in Fermoy (52°9'N, 8°14'W), a moderately drained sandy loam located at Teagasc
133 Johnstown Castle in Wexford (52°17'N, 6°30'W), and an imperfectly drained clay loam located at the
134 Agri-Food and Biosciences Institute (AFBI) in Hillsborough (54°45'N, 6°08'W). The climate on all sites
135 is temperate. Moorepark (MP) has an annual rainfall of 1202 mm and a mean annual temperature of
136 11.3°C (1981-2010, 30 year average), Johnstown Castle (JC) has an annual rainfall of 1037 mm and a
137 mean annual temperature of 10.4°C (1981-2010, 30 year average), and Hillsborough (HB) has an
138 annual rainfall of 944 mm and a mean annual temperature of 9.9°C (1981-2010, 30 year average).
139 Further soil and site details are listed in Table 1. Experimental period rainfall, ambient air and soil
140 temperature information were recorded at meteorological stations ca. 500 m from the experimental
141 sites.

142 The pasture at all sites was dominated by perennial ryegrass (*Lolium perenne* L.). Animals were
143 excluded from the sites for a minimum of six months prior to commencement of the experiment.

144 The study design consisted of three separate 365 day measurement periods in order to fully
145 assess seasonal effects on N_2O emissions from applied urine and dung. A split plot experimental
146 design was employed with site as the main plot factor, application season as the main split plot
147 factor and excreta treatment as the split-split plot factor. Five replicates of real urine, synthetic
148 urine, dung, and an untreated control were applied in April ('spring'), July ('summer'), and
149 September 2014 ('autumn'). For each season N_2O measurements were made from a single
150 urine/dung patch in each of the five replicates. Soil samples were taken from three replicates (blocks
151 1, 3, 5) where there were five additional urine/dung patches dedicated to soil sampling.

152

153 2.2 Treatments

Urine and dung were collected at JC and HB prior to each application, and the material from JC was also applied at MP. Urine and dung were collected a maximum of five days prior to application from lactating Holstein–Friesian dairy cows grazing at pasture, homogenised, and stored at 4°C for a maximum of five days, until application. Synthetic urine was prepared in the laboratory according to method R2 in Kool et al. (2006b). Samples of urine and dung were taken at application to determine total C and N, NH_4^+-N and NO_3^--N contents and dry matter (dung only). These data and calculated rates of N application for all treatments are shown in Table 2. At Hillsborough, sub-samples of bulked fresh and artificial urine were collected at application to determine urea, hippuric acid, allantoin, uric acid and creatinine content (Table 3). Briefly, sub-samples were diluted 1:3 with HPLC grade de-ionised water before addition of either 1 M sulphuric acid (to pH 3) or 9 µl chloroform to prevent sample degradation before analysis. Preserved samples were analysed using HPLC-UV (Phenomex Luna C 18 (2), 250 mm x 4.6 mm; pH 4, flow rate 1.0 ml min^{-1}) with the diode ray detector set at 218 nm.

Urine was applied inside the stainless steel static chamber bases (40 cm x 40 cm) to avoid seepage and run off from the patch at a loading rate of 2 L / (0.4 m) ^{2} = 12.5 L m^{-2}. The chamber base was left in place until the complete infiltration of the applied urine. Individual dung patches were 28 cm in diameter (0.062m^2), with 2 kg of fresh dung evenly applied at a loading rate of 33.3 kg m^{-2}. As the dung patch or the soluble nutrients from the patch spread over time as they would naturally in the field, thereby influencing the whole chamber base, application rate was calculated to be 12 kg m^{-2}.

2.3 N_2O sampling and analysis

The same N_2O sampling protocol was used at each site and season to enable direct comparison of results. The sampling protocol of Chadwick et al. (2014) was followed due to the high number of chambers deployed in this experiment (180). Most intensive measurements were taken for the first month after each application, with three sampling measurements per week, including sampling

immediately after treatment application and then one and three days later, before sampling frequency was reduced to 2, 1, 1 times a week in the following weeks, then once every two weeks until week 24, and thereafter once a month until the end of the experiment, with the final measurement taken on 365 days post application. Nitrous oxide was sampled on 33 occasions during the 12-month period using the closed static chamber technique (Mosier, 1989; de Klein and Harvey, 2012). Stainless steel 40 cm x 40 cm chambers were inserted at a minimum soil depth of 5 cm a minimum three days prior to treatment application. Chamber lids were 10 cm high creating an approximately 16 L headspace. Upon sampling, chambers were closed for 40 mins before withdrawing a 10 mL (20 mL in HB) gas sample through a rubber septum using a 10 mL (20 mL in HB) syringe fitted with a hypodermic needle. The sample was injected into a pre-evacuated 7 mL (12 mL in HB) screw-cap septum glass vial. The average of ten samples of ambient air, collected at each sampling, was used to determine T_0 for the N_2O flux calculation. Linearity of headspace N_2O concentrations was tested on each sampling occasion by collecting five samples at periodic intervals throughout a 60 minute period from five randomly selected chambers (Chadwick et al., 2014). Nitrous oxide concentrations were analysed using a gas chromatograph (GC) (Varian CP 3800 GC, Varian, USA at JC and MP; Bruker 450 GC, Bremen, Germany at HB) fitted with an electron capture detector (ECD). Gas sampling was performed between 10:00 and 13:00, according to good IPCC practice guidelines (IPCC, 2006). Hourly N_2O flux was calculated by linear regression of changes in N_2O concentration over time (Eq. 1).

$$F(hourly) = \left(\frac{\partial c}{\partial t}\right) \times \frac{M \times P}{R \times T} \times \left(\frac{V}{A}\right) \quad (1)$$

Where ∂c is the change in head space N_2O concentrations during the enclosure period in ppbv or µL L^{-1}, ∂t is the enclosure period expressed in hours, M is the molar weight of N in N_2O (28 g mol^{-1}), P and T the atmospheric pressure (Pa) and temperature (K) at the time of sampling, R the ideal gas constant (8.314 J K^{-1} mol^{-1}), V the headspace volume of the closed chamber (m^3) and A the area covered by the collar of the gas chamber (ha).

206 Calculated hourly N_2O flux was assumed to be representative of the average flux of the day
207 and was subsequently used to calculate daily N_2O flux (Blackmer et al., 1982; de Klein et al., 2003).
208 Cumulative N_2O emissions were calculated by linear interpolation of daily fluxes (de Klein and
209 Harvey, 2012). The N_2O emission factor (EF_3-PRP; N_2O-N emitted as % of dung or urine N applied) for
210 each treatment was calculated using cumulative N_2O emission following Eq. (2):
211
212 $$EF_3 = \frac{N_2O\ (Treatment) - N_2O\ (Control)}{N\ applied} \times 100\% \quad (2)$$

213 Where N_2O (Treatment) is cumulative N_2O emission (kg N_2O-N ha^{-1} yr^{-1}) for the dung or urine
214 treatment, N_2O (Control) is cumulative N_2O emission (kg N_2O-N ha^{-1} yr^{-1}) for the control, and N
215 applied is annual N application rate in kg ha^{-1} yr^{-1}.
216
217 2.4 Soil sampling and analysis
218 Soil was sampled on 14 occasions during each 12-month measurement period with most
219 intensive measurements (weekly) within the first month following application, after which sampling
220 intensity was reduced. Soil samples (0-10 cm) were collected with a soil auger from dedicated
221 patches in blocks 1, 3, and 5 and analysed for NH_4^+-N, NO_3^--N, and gravimetric moisture content.
222 Fresh soil samples were sieved (< 4 mm), extracted with 2 M KCl and mineral N concentration in the
223 extract determined using an Aquakem 600 discrete analyser at JC/MP and a SKALAR automated
224 continuous flow wet chemistry analysis (San++ System, Breda, The Netherlands) at HB. Soil samples
225 were dried at 105°C until constant weight for gravimetric moisture content. Soil bulk density (0-10
226 cm) was measured once for each season by a core method (USDA, 1999) in order to calculate
227 volumetric moisture content and water-filled pore space (WFPS). Separate soil cores (0-5 cm) were
228 used for measurement of soil field capacity (Šimůnek and Nimmo, 2005).
229
230
231

232 2.5 Statistical analysis

233 Statistical analysis of variance was performed using GenStat 16.2.0 (VSN International Ltd.,
234 Oxford, UK). Initially, all variables were analysed as a split-split plot ANOVA with Site as the main plot
235 factor, Season as the split-plot factor and Treatment as the split-split plot factor. Nitrous oxide was
236 the response variable. The treatment factors as described were used to analyse all variables in a full
237 factorial arrangement. Fisher's Least Significant Difference (LSD) test was used to assess pairwise
238 differences between individual treatments. In each case, the adequacy of the model was assessed by
239 examination of the appropriate residual plots. Nitrous oxide data were log transformed where
240 necessary prior to analysis in order to ensure normal distribution of residuals.

241 Cumulative N_2O emissions were modelled with stepwise multiple regression analysis using
242 parameters measured in the field using the GLMSELECT procedure in SAS 9.3 (© 2002–2010, SAS
243 Institute Inc., Cary, NC, USA, 2011). The explanatory variables were fitted as polynomial effects
244 allowing main effects, interactions and quadratic terms. Stepwise selection was used to assess
245 explanatory variables. The entry criterion was set to 0.15 to allow flexible entry with a retention
246 threshold of p=0.05. Robustness of the model was assessed by the Akaike Information Criterion
247 (AIC). Selected models were fitted with the MIXED procedure to allow residual checks to ensure that
248 the assumptions of the analysis were met. Nitrous oxide emissions were modelled based on the real
249 urine and synthetic urine treatments. Dung was not used in this analysis, despite the emissions
250 associated with this treatment often being significantly greater than those of the control treatment,
251 because measured emissions were low and relatively unresponsive in comparison to those of urine.
252 Modelled soil moisture deficit (SMD) was included in this multiple regression analysis (Schulte et al.,
253 2005). Soil moisture deficit (SMD) is a parameter describing the amount of rainfall needed to bring
254 the soil to field capacity. The model of Schulte et al. (2005) is used by the Irish Meteorological
255 Service to calculate SMD in Irish soils belonging to different drainage classes. Soil moisture deficit
256 values were calculated using a modified Penman–Monteith equation (Allen et al., 1998; Schulte et
257 al., 2005).

258

259 3. Results

260

261 3.1 Environmental and soil conditions

262

263 3.1.1 Temperature and Rainfall

264 Climatic conditions during the first 60 days of the experiment are presented in Figures 1-3, a-
265 c. Departures from long-term averages are provided in supplementary material (Fig. 4).Rainfall was
266 above the LTA in autumn in MP, in summer and autumn at JC and at all three seasons in HB, but
267 below in spring at JC and in spring and summer in MP. Temperature was above the LTA in spring and
268 summer in MP and in spring and autumn in JC, but below in autumn in MP, and at all three seasons
269 in HB.

270

271 3.1.2 Soil WFPS

272 Temporal patterns of WFPS during the first 60 days of the experiment are presented in
273 Figures 1-3, a-c. Overall, there was a significant site*season interaction on mean WFPS over the
274 whole experimental period ($P<0.05$). In summer JC and MP had the lowest WFPS, while in autumn
275 HB had the highest. Following a significant site*season interaction, simple effects were analysed.
276 Average WFPS in the spring for the first 60 days of the experiment was 60%, 82% and 71% in MP, JC
277 and HB, respectively. Site was significant in the spring experiment ($P<0.05$) with WFPS following the
278 trend MP<JC=HB. In the summer experiment, average WFPS was 44%, 48% and 57% at MP, JC and
279 HB, respectively (site significant at $P<0.05$, MP=JC<HB), while in the autumn experiment WFPS
280 averaged 53%, 55% and 74% at MP, JC and HB, respectively (site significant at $P<0.05$, MP=JC<HB).

281

282 3.1.3 Soil Mineral N

283 Temporal patterns of soil mineral N (NH_4^+-N, NO_3^--N) concentrations in the 0-10 cm soil
284 depth over the first 60 days post-application are presented in Figures 1-3, d-f. Profiles of soil mineral
285 N were typical. Applications of cow excreta (urine or dung) and synthetic urine increased mineral N
286 in all seasons and at all sites. Soil NH_4^+-N increased immediately following each treatment
287 application and generally returned to background levels within one month (spring MP and JC,
288 summer JC and HB), up to a maximum of three months (autumn HB). In general, the largest and
289 most prolonged NH_4^+-N concentrations occurred following the autumn application, however high
290 concentrations were also measured at HB after the spring application.
291 Concentrations of soil NO_3^--N returned to background levels within the same timeframe as
292 those of NH_4^+-N. Maximum NO_3^--N concentrations occurred later than those of NH_4^+-N and were
293 considerably lower. Nitrate concentrations were highest after the application of synthetic urine,
294 followed by the urine treatment and then the dung treatment, which reflected the N application
295 rates.
296 In 8 out of 9 cases of the site*season interaction soil NH_4^+-N and NO_3^--N concentrations were
297 significantly higher ($P<0.05$) from synthetic urine compared to urine treatment on at least one
298 sampling date. Significant differences occurred at times of peak concentrations, therefore soil NH_4^+-
299 N levels differed significantly shortly after treatment application, whereas this effect was delayed for
300 soil NO_3^--N.
301
302
303 3.2 Temporal N_2O emissions
304 Temporal fluxes of N_2O are shown in Fig. 1-3, g-i. While N_2O from control plots ranged between -
305 1.13 and 38.3 g N_2O-N ha^{-1} d^{-1} the application of cow excreta to grassland soil resulted in an
306 immediate large increase in N_2O emissions. Nitrous oxide followed a typical spike pattern of
307 emissions at all sites in the three experimental periods, however, the magnitude of the fluxes varied.
308 Peak mean daily fluxes recorded in spring, summer and autumn were 1458, 1105 and 2993 g N_2O-N

309 ha^{-1} d^{-1} respectively, which were all from the urine treatment at the imperfectly drained HB site.
310 Lowest daily fluxes were consistently observed from the well-drained MP soil. Peak emissions from
311 urine were between four and eight times lower from the JC (summer and autumn) and MP (spring)
312 soils, respectively, compared to the HB soil, in the respective seasons.

313 Peak daily N_2O emissions were highest in autumn, being 456, 767 and 2993 g N_2O-N ha^{-1} d^{-1} from
314 MP (urine), JC (synthetic urine) and HB (urine), respectively. Large N_2O fluxes were recorded on the
315 day of treatment application in all seasons at the HB site and in autumn from the MP soil, whereas
316 on other occasions fluxes on the day of application were low and increased in the following days.
317 Large fluxes on the day of application occurred at a range of soil moisture conditions, with WFPS
318 ranging between 38% and 72%. However, WFPS was comparable (ranging from 36% to 79%) in
319 instances where there was no response to excreta application on the day of application (i.e. JC site,
320 all seasons). In general, the largest N_2O fluxes following treatment application occurred in the
321 presence of rainfall. For example, large, sharp N_2O peaks from urine and synthetic urine at JC in
322 summer coincided with substantial rainfall events up to 30 mm over the first two weeks post-
323 application. Similar occurrences were observed at MP in autumn. In the absence of rainfall in the
324 first 10 days post-application the magnitude of the daily fluxes was lower, however, emissions were
325 more prolonged (e.g. at JC in spring or MP in summer). Assessment of linearity samples revealed
326 that non-linear accumulation of gas within the chamber headspace was <5% at all sites and seasons.
327 Linear equation was used in the N2O flux calculations.

328

329 3.3 Cumulative N_2O emissions

330 All cumulative losses of N_2O are shown in Table 4. Statistical analysis revealed a significant
331 treatment, site, and season interaction ($P<0.001$), therefore simple effects were analysed (by season
332 and by site).

333 Cumulative N_2O emissions from the dung treatment were low throughout all experimental periods
334 and in spring emissions ranged from 1.05 to 1.40 kg N_2O-N ha^{-1} yr^{-1}, which were not significantly

different from those of the control plots (0.65 – 0.76 kg N_2O-N ha^{-1} yr^{-1}). Cumulative emissions in summer ranged from 0.94 to 3.89 kg N_2O-N ha^{-1} yr^{-1} and in autumn they ranged from 1.25 to 7.01 kg N_2O-N ha^{-1} yr^{-1}, which were generally significantly larger than the control ($P<0.05$), apart from MP in summer. Cumulative N_2O emissions from dung were significantly higher at the HB site in the summer and autumn compared to the other sites and there was no significant seasonal effect elsewhere.

Application of urine universally produced significantly larger N_2O losses (2.77 – 43.1 kg N_2O-N ha^{-1} yr^{-1}) in comparison with the control and dung ($P<0.05$). No clear seasonal effect was observed at the MP or JC sites with only N_2O from the autumn application at JC significantly larger than the summer application. However, a large seasonal effect was observed at the HB site, where emissions followed the order spring < summer < autumn, which is in line with the N application rate for this treatment. Cumulative emissions from urine at the MP site were consistently lower than at the HB site. Similarly to real urine, synthetic urine produced large cumulative N_2O emissions ranging from 2.26 to 44.4 kg N_2O-N ha^{-1} yr^{-1}. Seasonal effects varied with site. There was no significant difference between seasons at JC. At MP cumulative N_2O emissions post autumn application were lower than in spring and summer ($P<0.05$), whereas at HB all seasons differed significantly with summer< spring < autumn.

3.4 N_2O emission factors

The EFs from dung ranged from -0.02% to 1.48% and were consistently lower and less variable (SEM 0.16%) than urine (SEM 0.48%) or synthetic urine (SEM 0.39%). The lowest EF calculated for the dung treatment was negative indicating that the N_2O emitted from the dung plots was numerically lower than that from control plots, however, this was not statistically significant (Table 5). There was a significant ($P<0.05$) seasonal effect with EFs from dung overall sites in autumn being higher (0.52%) than in summer (0.21%) or spring (0.09%) (Table 6).

359 The EFs from urine ranged from 0.30% to 4.81%. Similarly to dung the EFs from urine, overall
360 sites, were significantly higher in autumn (1.56%) compared with summer (0.71%) or spring (0.67%).
361 The EFs from synthetic urine ranged from 0.13% to 3.82% and when compared at each site, EFs did
362 not differ significantly from urine, despite the difference in composition (Table 3). There was a
363 significant site x treatment interaction ($P<0.01$) with EFs for dung, urine and synthetic urine being
364 significantly higher at the HB site compared to the other two sites. Overall, only two of the 27
365 measured EFs were higher than the IPCC default value of 2% for cattle grazing returns. These were
366 both recorded at HB in the autumn, where the EFs for synthetic urine and real urine were 3.82% and
367 4.81%, respectively.
368
369 3.5 Drivers of N_2O emissions
370 Drivers of N_2O emission were assessed using a stepwise multiple regression analysis of the two
371 urine treatments (real urine and synthetic urine) and are shown in Table 7 a and b. The multiple
372 regression analysis including weather and soil parameters showed that 72% of the variation in N_2O
373 emissions ($P<0.005$) could be explained by cumulative rainfall five days prior to treatment
374 application, soil clay content and N application rate (Table 7a). Second run of the multiple
375 regression analysis using only weather data predicted cumulative rainfall for the five days prior to
376 application, mean soil temperature in the seven days prior to application, and mean soil moisture
377 deficit for the five days post-application (Table 7 b and supplementary information Table 8) to be
378 responsible for 72% of the variation ($P<0.005$). The relationship with rainfall was described by a
379 squared term rather than a linear fit. Including squared terms in the statistical model allowed for
380 deviations from the simplest model with just the main effects included.
381
382
383 4. Discussion
384

385 4.1 N_2O emissions

386 Similarly to previous studies (Maljanen et al., 2007; Luo et al., 2008; van der Weerden et al.,
387 2011; Krol et al., 2015), N_2O emissions increased rapidly in response to urine application. The initial
388 peak of N_2O is reported to be driven by denitrification of the indigenous soil nitrate pool, stimulated
389 by an increase in water soluble carbon released as an effect of increased pH during urea hydrolysis,
390 lysing of microbial cell membranes or slaking of soil aggregates (Monaghan and Barraclough, 1993;
391 Lambie et al., 2012, Burchill et al. 2014). In fact, Wachendorf et al. (2008) established that 75% of
392 urine-induced N_2O originated from the indigenous soil mineral N pool rather than applied urinary N.
393 This rapid N_2O emission on the day of urine application was particularly noticeable at the HB and MP
394 sites.

395 In most cases N_2O remained elevated for approximately 60 days, however in autumn on the
396 imperfectly drained HB soil, emissions from the urine and synthetic urine treatments remained
397 higher than the control for approximately 130 and 200 days, respectively. Cumulative N_2O emissions
398 on both the synthetic urine and real urine treatments were substantially higher at the HB site in
399 spring, summer and autumn, compared to the same time period at the other two sites. This
400 reflected the higher WFPS of the imperfectly drained HB soil, particularly following the autumn
401 application (Fig. 3 a-c). At HB the higher N content of real urine in autumn compared to spring and
402 summer could be attributed to seasonal differences in the dairy cow diet. Quality of pasture is
403 subject to seasonal changes, with grass digestibility decreasing in autumn and crude protein content
404 (CP) increasing after a drop in the summer months (McCarthy et al., 2012). This leads to lower
405 utilisation of the ingested N by grazing animals and higher N excretion (O'Donovan et al., 2011;
406 Dijkstra et al., 2013). Furthermore, grass growth and as a consequence plant uptake of applied urine
407 N declines in autumn (Corré et al., 2014) leaving more mineral N susceptible to N_2O loss.

408 Selbie et al. (2014) reported a non-linear relationship between N_2O flux and increasing N
409 application rate. Despite the N application rate from synthetic urine being considerably higher than
410 from real urine, cumulative N_2O emissions were only significantly higher on two occasions (following

411 spring application and JC and HB).The urea-N content of the synthetic urine was consistently higher
412 than in real urine, which may have led to greater ammonia volatilisation. High urea-N content can
413 also lead to N_2 production as urine patches create optimal conditions for co-denitrification (Selbie et
414 al. 2015).

415 The period of enhanced N_2O emissions corresponds well with other studies. Van der Weerden et
416 al. (2011) reported enhanced emissions over 12-173 days from a variety of well and poorly drained
417 soils, and Bell et al. (2015) observed emissions returning to background levels within 2-3 months
418 after application on a free draining soil. However, de Klein et al. (2003) reported elevated emissions
419 lasting between four and 18 months depending on region, soil type and soil drainage properties.

420 Cattle dung deposition also resulted in enhanced N_2O emissions that were significantly different
421 from those of the control in five out of nine cases. However, cumulative emissions were lower than
422 those of urine, and showed a slower response following application. Urine patches were
423 characterised by very high N application rates of up to 1240 kg N ha^{-1} which had a large impact on
424 soil mineral N. Moreover, the majority of N in urine converted quickly to the mineral form, which is
425 readily available for microbial processes leading to N_2O formation. Levels of soil mineral N were
426 significantly lower beneath dung patches, which resulted in lower N_2O emissions. This was due to a
427 lower N application rate as this form of excreta is characterised by a relatively low N content in
428 comparison to urine. The vast majority of N in dung is in an organic form (Haynes and Williams,
429 1993) which, combined with high levels of organic C in dung, may lead to temporary N
430 immobilisation during C decomposition upon application. Furthermore, the high dry matter content
431 of dung can cause drying and crusting of material in dry weather conditions, which may affect the
432 rate of N infiltration into the soil (van der Weerden et al., 2011).

433 In all seasons and at all sites, N_2O fluxes followed a large increase in the soil NH_4^+-N pool. Peaks
434 in soil NO_3^--N concentrations occurred later than those of NH_4^+-N and were considerably lower,
435 probably due to plant uptake, N immobilisation and high N_2 emissions. Nitrification is reported to be
436 an important source of N_2O on occasions when the increased flux precedes changes in the soil NO_3^--

437 N pool Bell et al., 2015). However, in high WFPS conditions such as at JC in spring or HB in autumn
438 (79% and 72%, respectively) denitrification is considered to be the main N_2O loss pathway. This is
439 supported by the secondary N_2O peaks occurring after the peak in the soil NO_3^--N pool.
440
441 4.2 N_2O emission factors
442 The average EF over all sites for real urine was 1.18% (ranging from 0.30% to 4.81%) and for
443 synthetic urine was 1.01% (ranging from 0.13% to 3.82%), which were in line with previous studies.
444 Allen et al. (1996) reported EFs of between 0.0 and 2.3% for a grassland site in the south-west of the
445 UK, while studies in New Zealand found EFs between 0.5 % from a well-drained stony silt loam and
446 3.7% from a moderately-drained silt loam (de Klein et al.,2003). Van der Weerden et al. (2011)
447 reported EFs of 0.05 and 0.94% from a well-drained silt loam in Hawkes Bay and a poorly drained silt
448 loam in Waikato in spring, respectively, while Clough et al. (1996) reported the EF below 1% from
449 peat soil and 3% from mineral soil, and later below found EFs below 2% from various soil types
450 (Clough et al., 1998). The recent study of Bell et al. (2015) found N_2O EFs from urine to be 0.20 and
451 1.07% from a sandy to sandy-loam soil in Scotland in spring and summer, respectively. In the current
452 study, soil type had an effect on both real and synthetic urine EFs, with EFs from well-draining soils
453 significantly lower than those on imperfectly drained soils. Synthetic urine, being made to a standard
454 recipe, was used to assess both soil and seasonal effects. There was a large seasonal effect on N_2O
455 emission from synthetic urine where EFs were overall lowest in summer (0.51%), significantly higher
456 in spring (0.91%), and highest in autumn (1.09%). Synthetic urine does not fully mimic real urine
457 composition, especially with respect to minor constituents (Table 3), which vary considerably with
458 diet and for this reason van Groenigen et al., (2005) did not recommend using it to determine
459 emission factors. However, in the current study, EFs from synthetic urine were similar to urine, when
460 compared at each site and therefore it appears to be a reasonable proxy for real urine.
461 Dung EFs were consistently lower than urine, in agreement with other studies (van der Weerden
462 et al., 2011; Dijkstra et al., 2013; Lessa et al., 2014, and Bell et al., 2015). The average EF for dung

463 overall sites was 0.31% (± 0.16%). These EFs are comparable to those reported in the literature of
464 0.02 to 0.40% for grazed hill land in New Zealand (Luo et al., 2013a), 0.10 to 0.20% for grassland in
465 Scotland (Bell et al., 2015), or 0.00 to 0.16% in Brazilian pastures (Lessa et al., 2014) and are in line
466 with the EF_{3DUNG} of 0.25% used in New Zealand for calculating national greenhouse gas inventories
467 (Saggar et al., 2015). The dung EF of 1.48% at the HB site in autumn had a large effect as the average
468 of the remaining EFs was only 0.16%. However, as previously described, conditions in autumn in this
469 imperfectly drained soil were favourable towards denitrification, leading to high N_2O losses. There
470 was a large seasonal effect on N_2O emissions from dung where EFs were significantly higher in
471 autumn than in spring or summer. Dung EFs were also higher on the imperfectly-drained soil
472 compared to the better drained soils. As dung EFs are considerably lower than urine, there is
473 potential to reduce N_2O emissions through manipulating N excretion towards the dung fraction.
474 Partitioning of excretal N between urine and dung can be affected by diet, mainly by manipulating N
475 intake. Therefore dietary manipulation such as supplementing pasture forage with condensed
476 tannins and/or maize or cereal silage, or sucrose can lower the N concentration in urine (Jarvis et al.,
477 1996; Oenema et al., 1997) and increase the proportion of excretal N in the form of dung (Valk,
478 1994; Howard et al., 2007).

479 Bell et al. (2015) found lower EFs from animal excreta in comparison with the IPCC default value
480 of 2% and suggested that this should be reduced for countries with temperate climates, such as the
481 UK. Results of the current study, with an average EF of 0.31% from dung, 1.18% from urine and
482 1.01% from synthetic urine, and an overall average of 0.87%, support this view. This has practical
483 implications for the national N_2O inventory and any future mitigation strategies. Variation in EFs
484 between type of excreta, soil type and season indicate that use of the IPCC default EF is not
485 appropriate for temperate grasslands and therefore the study of Bell et al. (2015) and the current
486 experiment support recommendations to adopt country-specific N_2O EFs for grazing returns and
487 support the disaggregation of EFs by excretal type.

Two of the EFs calculated from the current study were above the IPCC default EF of 2% and both of these occurred from urine treatments on the imperfectly drained soil under high denitrifying conditions in autumn. In contrast, EFs from well-drained soils were all below 2%. This highlights practical concerns in terms of grazing management on different soil types. These results suggest that N_2O emissions can be reduced by avoiding grazing imperfectly drained soils in wet spring and autumn conditions. Improving soil drainage of imperfectly drained soils may extend grazing season and mitigate N_2O (Touhy et al., 2016).

4.3 Drivers of N_2O emissions

The results of this study suggest that the extent of N_2O emissions was strongly influenced by soil and weather conditions shortly before and after deposition of excreta (r^2=72 %) (Table 7 a). Nitrous oxide increased with increasing level of precipitation during the five days prior to application of excreta. Rainfall is a proxy of soil moisture which is known to be one of the main parameters responsible for N_2O emission (Dobbie and Smith., 2001; del Prado et al., 2006; Schaufler et al., 2010; Luo et al., 2013b). Soil moisture is influenced by soil texture and drainage properties and soil clay content was another parameter that influenced N_2O fluxes. Following similar amounts of precipitation, soils with higher clay content respond to rainfall more slowly and the soil moisture remains higher for longer, whereas moisture in light-textured, free draining soils closely follow rainfall patterns, quickly increasing and decreasing afterwards. The imperfectly drained soil in HB consistently received more rainfall in the first 60 days following each seasonal application than the LTA during the experimental periods, while the other two soils received mixed levels of rainfall in relation to the LTA (drier springs and wetter autumns). This was reflected in WFPS which remained high for most of the experimental periods at HB, and was less variable in comparison with the other two soils. In fact, the WFPS at HB ranged between 60% and 80 % for at least 50 days post-application in both spring and autumn. High WFPS restricted oxygen concentration in soil leading to anaerobic conditions stimulating denitrification which is believed to be a major source of large N_2O losses in

514 the HB soil. These results relate well to the study of de Klein et al. (2003), who found highest N_2O
515 emissions generated from poorly drained silt loam soil amended with urine, even under rainfall
516 conditions lower than on the other sites. However large N_2O emissions also occurred shortly after
517 application, even in low WFPS conditions, following a rainfall event, which is in line with findings of
518 Bell et al. (2015) who found the highest N_2O emissions in summer (low WFPS). According to Carter
519 et al. (2007) high N_2O at low WFPS (at approximately 45%) could be due to equal contributions of
520 nitrification and denitrification to emissions. The maximum N_2O emissions throughout the
521 experiment were seen at WFPS 70-80%, mainly in spring and autumn when soils were at their
522 wettest which is similar to findings of Luo et al. (2008) and Di et al. (2014). However, cumulative N_2O
523 emissions showed a weak correlation with WFPS on its own, possibly due to the large variability in
524 the data and rainfall was a more suitable proxy of emissions in this case. The quadratic term used in
525 the model in relation to rainfall indicates a curved relationship, possibly a flattening increase or a
526 decrease in N_2O emission above a certain level of precipitation, similar to the bell-shaped
527 relationship between N_2O and WFPS described by Bouwman (1998).

528 As expected, the magnitude of the N_2O loss also depends on the rate of N applied, which varied
529 markedly between sites and seasons. Higher N application rate translated into more substrate in the
530 soil (Figs 1-3, d-f) available for nitrification and denitrification and was subsequently responsible for
531 higher N_2O emissions. This effect has been widely reported in the literature with regard to synthetic
532 fertiliser (Bouwman et al., 2002), synthetic urine (de Klein et al., 2014), real urine (Selbie et al., 2014)
533 and organic manure (Meade et al., 2011).

534 A suite of parameters tested in the stepwise multiple regression analysis was then narrowed
535 down strictly to weather data available through weather forecasts (Table 6 b). The analysis used
536 weather data ranging from ten days prior, to ten days post-treatment; and resulted in a statistical
537 model potentially useful for predicting conditions of high N_2O loss and guiding management
538 decisions. Similarly to above, N_2O flux was mostly controlled by cumulative rainfall for the five days
539 prior to application, but also mean soil temperature in the seven days prior to application, and mean

soil moisture deficit for the five days post-application (r^2=72%) (Table 7 b and 8). The effect of temperature on N_2O emissions has been extensively described in the literature (Mosier et al., 1998; Dobbie and Smith, 2001; Luo et al., 2013b). A study of Abdalla et al. (2009) found a very high sensitivity of denitrification to temperature and low activation energy for the process in Irish sandy loam pasture soil. Inclusion of SMD in the statistical model is complementary to precipitation, with low N_2O emissions at low levels of precipitation and high SMD, and N_2O increasing with higher rainfall and lower SMD. The highest cumulative N_2O coincided with the zero SMD indicating saturation of the soil. As a means of N_2O mitigiation soil moisture deficit could be used as a decision support tool for farmers to indicate times that grazing should be avoided through a more dynamic decision process for housing of animals. Improving soil drainage may also reduce N_2O emissions through increasing SMD, however care is needed due to the potential of enhancing CO_2 respiration.

5. Conclusions

The application of cattle urine, and to a smaller extent cattle dung, increased N_2O emissions from pasture soils, with peak losses occurring within the first 60 days of application. The average N_2O emission factor was 0.31% and 1.18% for cattle dung and urine respectively, which were both considerably lower than the IPCC default value of 2%. These results support the disaggregation of EFs by excreta type. Consequently, calculation of N_2O emissions from grazing returns should be weighted accordingly to the partitioning of forms of excreta and this will require better activity data to account for variable animal types and diets. N_2O emissions can be predicted by rainfall and temperature before and soil moisture deficit after excreta application. Greatest N_2O losses and highest EFs in this study were associated with high rainfall and high soil moisture conditions, conducive to denitrification, on an imperfectly drained site. There is potential for a decision support tool to reduce N_2O emissions to be developed by modifying grazing management based on these parameters. High variability of N_2O emissions with soil type and season suggest that using a

universal EF in national GHG inventories is inappropriate and application of country, or if possible soil and season specific values, should be used.

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769 Table 1 Physical and chemical soil characteristics at 0-10 cm depth (n=5).

Site	MP	JC	HB
Soil Texture	Sandy Loam	Sandy Loam	Clay Loam
Drainage	good	moderate	imperfect
Sand (%)	57.8	52.9	47.1
Silt (%)	28.2	33.2	31.9
Clay (%)	14.1	13.9	21.0
LOI (%)	7.9	7.3	12.4
pH	5.4	5.5	5.8
Total C (%)	3.02	3.16	4.95
Total N (%)	0.32	0.30	0.47
CEC (cmol kg^{-1})	18.4	15.6	23.6
Field capacity (%)	30.3	35.8	46.1

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772 Table 2 N application rate and chemical characteristics of applied excreta.

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Site	Season	Treatment	Application rate (kg N ha^{-1})	Total N (g N L^{-1} or kg)	Urea N (mg N L^{-1})	Nitrate N	Ammonium N
MP[1]	spring	Urine	660	5.28	1335.0	0.0	2517.0
		S urine*	1166	9.33	7851.0	0.0	157.0
		Dung	490	3.92	-	-	-
	summer	Urine	774	6.19	4308.4	0.0	1564.6
		S urine	1218	9.74	9636.4	0.0	57.9
		Dung	469	3.75	-	-	-
	autumn	Urine	739	5.91	4902.6	4.1	894.6
		S urine	1194	9.55	9708.0	4.4	34.9
		Dung	420	3.36	-	-	-
JC[2]	spring	Urine	638	5.10	3688.0	0.0	290.0
		S urine	1139	9.11	7559.0	0.0	72.0
		Dung	490	3.92	-	-	-
	summer	Urine	725	5.80	3495.0	34.1	2280.5
		S urine	1181	9.45	8992.0	10.4	34.0
		Dung	469	3.75	-	-	-
	autumn	Urine	718	5.74	4704.4	0.0	870.4
		S urine	1210	9.68	9701.3	0.0	35.8
		Dung	420	3.36	-	-	-
HB[3]	spring	Urine	507	4.06	366.0	13.7	3155.0
		S urine	1229	9.83	8100.0	122.9	44.5
		Dung	280	2.24	-	0.6	325.8
	summer	Urine	840	6.72	1650.0	20.6	5193.3
		S urine	1240	9.92	9172.5	119.3	109.1
		Dung	651	5.21	-	1.1	676.3
	autumn	Urine	897	7.17	2872.5	40.9	2650.0
		S urine	1214	9.71	7257.4	140.8	116.8
		Dung	441	3.52	-	0.7	469.2

774 [1]Moorepark site
775 [2]Johnstown Castle site
776 [3]Hillsborough site
777 *S urine stands for 'Synthetic urine' treatment
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780 Table 3 Minor constituents of urine applied at the Hillsborough site.

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Site	Season	Treatment	Allantoin (mg N L^{-1})	Creatinine	Uric acid	Hippuric acid
HB[3]	spring	urine	<100	90.9	62	33.8
		S urine	1457.7	317.8	76.2	515
	summer	urine	<100	<30	20	<30
		S urine	1263.4	321.6	79.6	522.3
	autumn	urine	<100	83	56.1	<30
		S urine	1366	330.4	80.5	540

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788 [3]Hillsborough site

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792 Table 4 Mean cumulative N_2O emissions (kg N $ha^{-1}yr^{-1}$) for 365 days of measurements by site x season x treatment (n=3). All averages reported are
793 calculated from back-transformations of total emissions.

		Control			Dung			Urine			Synthetic urine		
	Spring	0.76	B	ab	1.05	B	b	2.77	A	d	4.56	A	d
MP[1]	Summer	1.04	B	a	0.94	B	b	3.05	A	d	4.49	A	d
	Autumn	0.62	C	abc	1.25	B	b	2.79	A	d	2.26	AB	e
	Spring	0.66	C	ab	1.17	C	b	4.61	B	cd	9.09	A	c
JC[2]	Summer	0.43	C	bc	1.09	B	b	2.86	A	d	5.03	A	cd
	Autumn	0.32	C	c	1.36	B	b	8.63	A	bc	7.54	A	cd
	Spring	0.76	C	ab	1.40	C	b	6.83	B	c	22.3	A	b
HB[3]	Summer	0.76	C	ab	3.89	B	a	14.3	A	b	8.68	A	c
	Autumn	0.59	C	abc	7.01	B	a	43.1	A	a	44.4	A	a

794 Means followed by same letter are not significantly different at $P<0.05$
795 Upper-case lettering refers to comparisons within rows
796 Lower-case lettering refers to comparisons within columns
797 [1]Moorepark site
798 [2]Johnstown Castle site
799 [3]Hillsborough site
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Table 5 Emission factors (%) by site x season x treatment (n=3).

		Dung		Urine		Synthetic urine	
MP[1]	Spring	0.03	(0.04)	0.32	(0.09)	0.34	(0.10)
	Summer	-0.02	(0.03)	0.31	(0.14)	0.34	(0.13)
	Autumn	0.13	(0.04)	0.30	(0.09)	0.13	(0.02)
JC[2]	Spring	0.06	(0.06)	0.65	(0.26)	0.84	(0.35)
	Summer	0.16	(0.06)	0.34	(0.06)	0.43	(0.11)
	Autumn	0.24	(0.06)	1.16	(0.10)	0.59	(0.05)
HB[3]	Spring	0.15	(0.18)	1.12	(0.26)	1.79	(0.31)
	Summer	0.54	(0.22)	1.63	(0.39)	0.82	(0.33)
	Autumn	1.48	(0.21)	4.81	(0.97)	3.82	(0.98)
	Average	0.31	(0.16)	1.18	(0.48)	1.01	(0.39)

Values in brackets are the SEM

[1]Moorepark site

[2]Johnstown Castle site

[3]Hillsborough site

Table 6 Mean N_2O emission factors (%) by site x season, site x treatment and season x treatment.

Site x Season		EF (%)	Site x Treatment		EF (%)	Season x Treatment		EF (%)
	Spring	0.22 *ab*		Dung	0.04 *a*	Spring	Dung	0.09 *a*
MP[1]	Summer	0.21 *ab*	MP[1]	Urine	0.32 *bc*		Urine	0.67 *bc*
	Autumn	0.18 *a*		Synthetic Urine	0.27 *b*		Synthetic Urine	0.91 *cd*
	Spring	0.49 *bc*		Dung	0.16 *ab*	Summer	Dung	0.21 *a*
JC[2]	Summer	0.32 *ab*	JC[2]	Urine	0.70 *d*		Urine	0.71 *bc*
	Autumn	0.62 *cd*		Synthetic Urine	0.61 *cd*		Synthetic Urine	0.51 *b*
	Spring	0.91 *d*		Dung	0.64 *cd*	Autumn	Dung	0.52 *b*
HB[3]	Summer	0.95 *d*	HB[3]	Urine	2.21 *e*		Urine	1.56 *e*
	Autumn	3.12 *e*		Synthetic Urine	1.91 *e*		Synthetic Urine	1.09 *d*
SEM		1.07			1.07			1.05

Means followed by same letter not significantly different at P<0.05

[1]Moorepark site

[2]Johnstown Castle site

[3]Hillsborough site

Table 7 Full fixed model of multiple regression analysis for cumulative N_2O flux (g N_2O-N ha^{-1} yr^{-1}) from urine and synthetic urine treatments using soil and weather data (a), and weather data only (b).

a) Parameter	DF	Estimate	Std. Error	Adjusted R-Square	t	F	Pr > F
1	1	-383.9	181	0.49	-2.12	87.79	<0.0001
1^2	1	15.99	3.09	0.69	5.18	9.17	0.003
2	1	1443	313	0.71	4.62	5.22	0.025
3	1	7.780	3.62	0.72	2.15	4.63	0.034

Parameters:

1 Cumulative precipitation five days prior application
2 1^2 + soil clay content
3 2 + N application rate

b) Parameter	DF	Estimate	Std. Error	Adjusted R-Square	t	F	Pr > F
1	1	-0.12	0.02	0.50	-5.24	89.12	<.0001
2	1	-0.11	0.03	0.68	-3.74	5.68	0.0193
1 ^2	1	0.00	0.00	0.70	7.83	5.12	0.0262
3	1	0.07	0.02	0.72	4.09	8.57	0.0044

Parameters:

1 Cumulative precipitation five days prior application
2 1^2 + soil temperature seven days prior application
3 2 + soil moisture deficit five days post-application

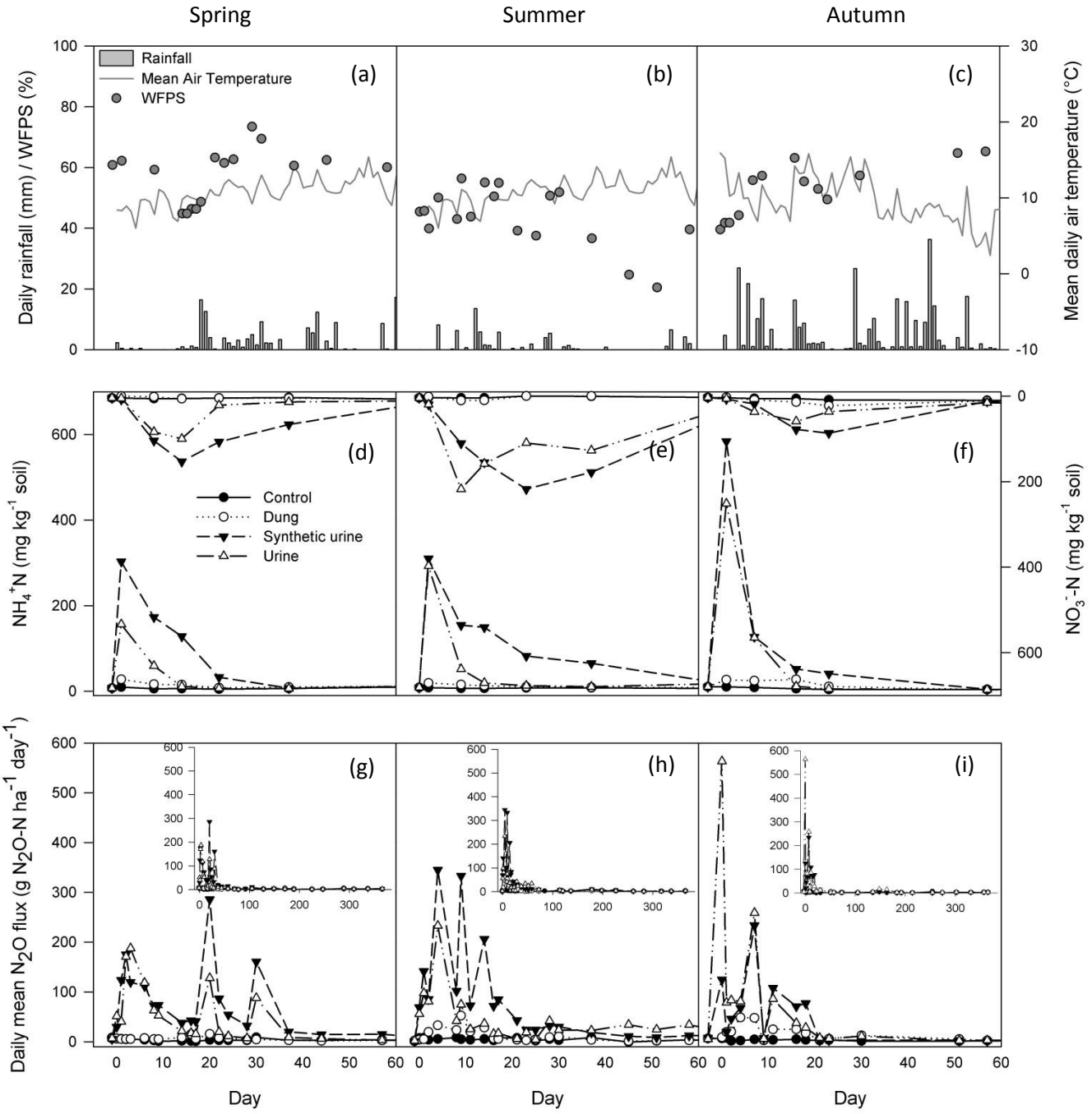

Figure 1. The variation in daily N_2O emissions, soil mineral N (NH_4^+-N and NO_3^--N shown as mirror image), and daily rainfall, mean daily air temperature and water-filled pore space (WFPS) during the first 60 days of measurements following dung and urine application at Moorepark site in spring (a, d, g), summer (b, e, h), and autumn (c, f, i). Inset graphs show daily N_2O emissions over 365 days. Pooled standard error of the mean for NH_4^+-N and NO_3^--N, respectively, was 10.1 and 7.2 (d), 15.6 and 20.0 (e), and 16.2 and 7.7 (f), while pooled standard error of the mean for N_2O was 11.9 (g), 18.6 (h), and 8.8 (i).

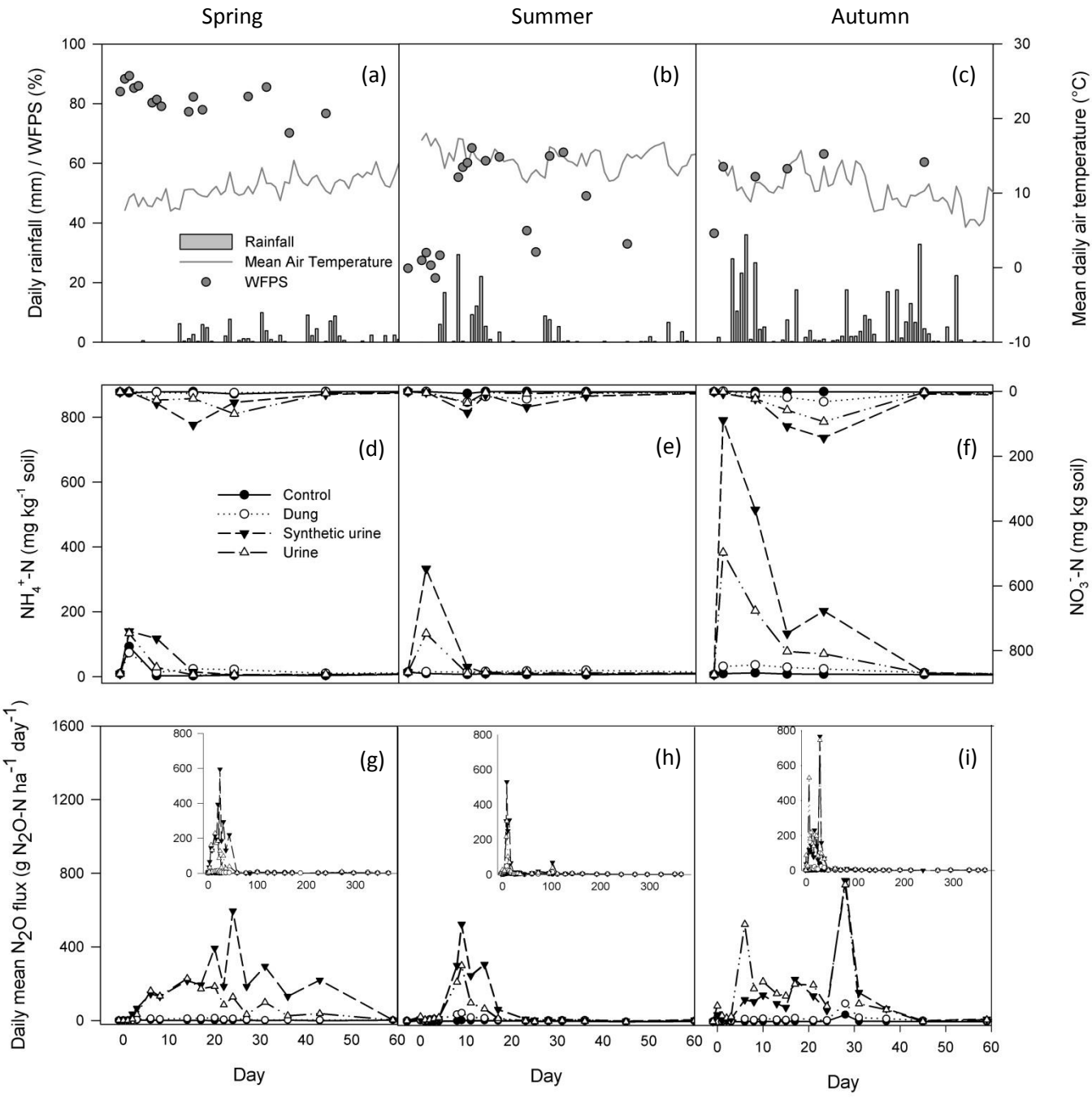

Figure 2. The variation in daily N_2O emissions, soil mineral N (NH_4^+-N and NO_3^--N shown as mirror image), and daily rainfall, mean daily air temperature and water-filled pore space (WFPS) during the first 60 days of measurements following dung and urine application at Johnstown Castle site in spring (a, d, g), summer (b, e, h), and autumn (c, f, i). Inset graphs show daily N_2O emissions over 365 days. Pooled standard error of the mean for NH_4^+-N and NO_3^--N, respectively, was 5.9 and 8.2 (d), 26.4 and 6.3 (e), and 41.5 and 6.2 (f), while pooled standard error of the mean for N_2O was 41.0 (g), 24.9 (h), and 25.9 (i).

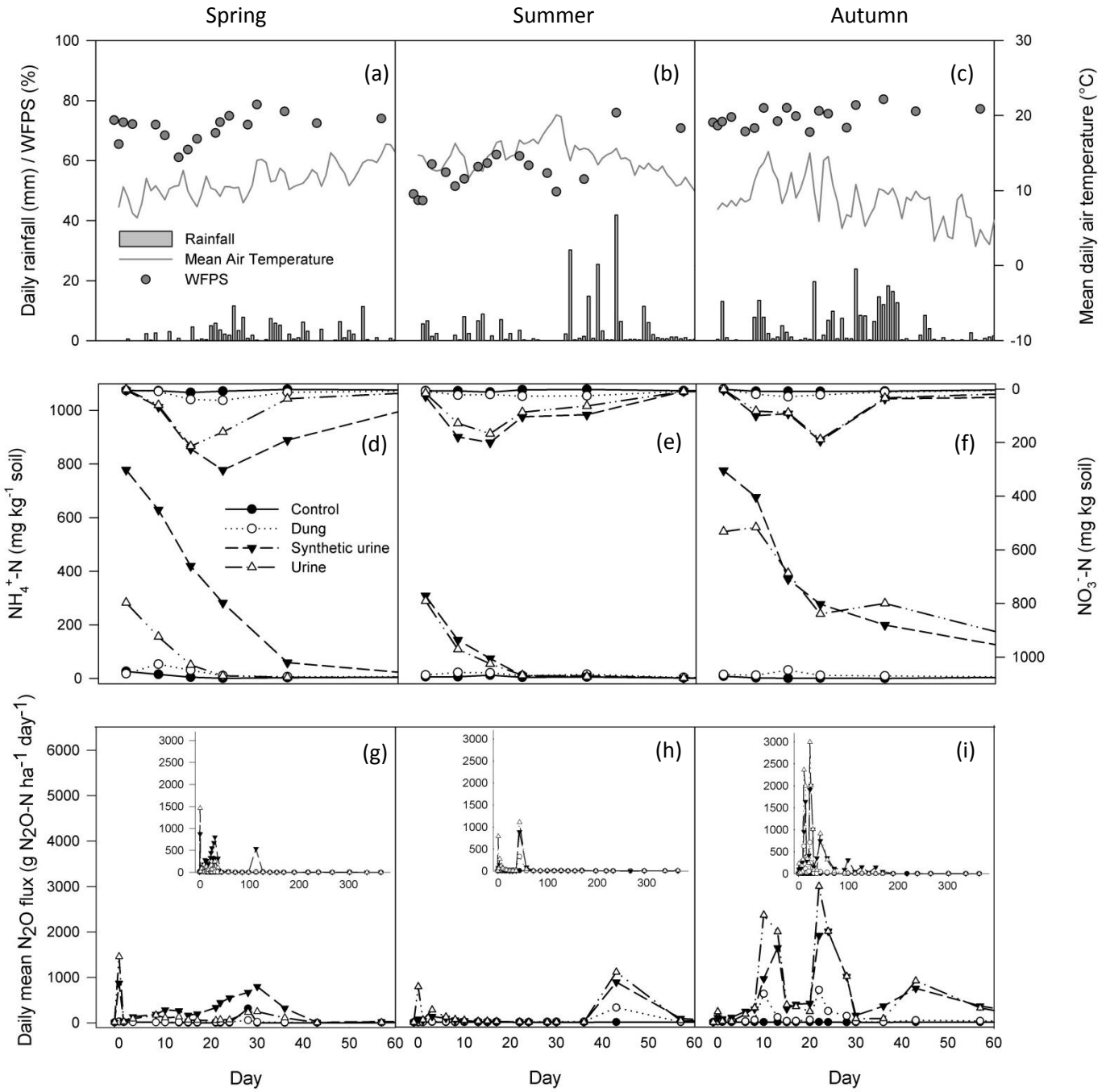

Figure 3. The variation in daily N_2O emissions, soil mineral N (NH_4^+-N and NO_3^--N shown as mirror image), and daily rainfall, mean daily air temperature and water-filled pore space (WFPS) during the first 60 days of measurements following dung and urine application at Hillsborough site in spring (a, d, g), summer (b, e, h), and autumn (c, f, i). Inset graphs show daily N_2O emissions over 365 days. Pooled standard error of the mean for NH_4^+-N and NO_3^--N, respectively, was 18.6 and 10.7 (d), 13.8 and 10.2 (e), and 45.2 and 8.7 (f), while pooled standard error of the mean for N_2O was 87.2 (g), 40.9 (h), and 180.0 (i).

Supplementary information

Table 8 Weather parameters included in the multiple regression analysis and corresponding with the 60 days temporal N_2O figures 1-3 g-i.

		5 days prior to application	7 days prior to application	0 - 5 days post-application	0 - 60 days post-application		
Site	Season	Precipitation*	Soil temperature[+]	SMD[++]	Precipitation*	Soil temperature[+]	SMD[++]
	Spring	15.4	11.0	4.3	139.1	13.2	7.5
MP[1]	Summer	14.0	20.9	15.7	74.1	16.7	25.1
	Autumn	5.4	15.5	1.0	318.8	10.3	0.4
	Spring	29.6	10.6	6.0	95.2	13.3	11.9
JC[2]	Summer	0.0	23.4	5.6	142.8	17.1	20.9
	Autumn	1.0	15.4	0.4	349.2	10.6	0.4
	Spring	4.2	9.2	7.5	122.0	11.8	2.0
HB[3]	Summer	13.8	12.5	20.4	214.2	15.1	8.5
	Autumn	58.6	12.8	0.0	248.2	9.5	0.4

* Cumulative precipitation

[+]Average soil temperature at 0-5cm

[++] Average SMD

[1]Moorepark site

[2]Johnstown Castle site

[3]Hillsborough site

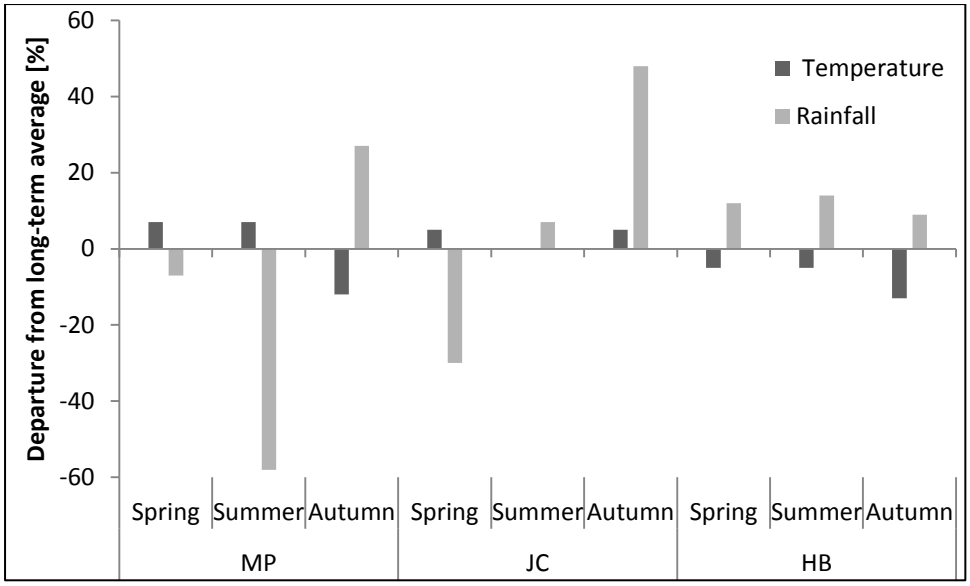

Figure 4. Departure of temperature and rainfall from a long-term average for Moorepark (MP), Johnstown Castle (JC) and Hillsborough (HB) sites at all three seasons during the experimental period.