

Scotland's Rural College

How do emission rates and emission factors for nitrous oxide and ammonia vary with manure type and time of application in a Scottish farmland?

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Abstract

The use of livestock manure as an organic fertiliser on agricultural land is an attractive alternative to synthetic fertiliser. The type of manure and the timing and method of application can however be crucial factors in reducing the extent of nitrogen lost from the system. This is important not only to enhance crop production, but in controlling gaseous emissions, including nitrous oxide (N₂O) and ammonia (NH₃). Emissions of N₂O and NH₃ were measured for 12 months from two experiments at an arable site in Scotland, to determine the effect of manure type and the timing (season) of application. Emission factors (EFs) were calculated for each manure applied in each season, and compared to IPCC standard EFs of 1% for N₂O and 20% for NH₃. Cattle farmyard manure, broiler litter, layer manure, and cattle slurry by surface broadcast and trailing hose application were applied to one experiment in October 2012 (autumn applications) and one in April 2013 (spring applications). Experimental areas were sown with winter wheat (*Triticum aestivum*) and manures applied at typical rates. Crop yield was recorded to allow calculation of N₂O and NH₃ emission intensities. Mean annual N₂O emissions across all manure treatments were greater from autumn (2 kg N₂O-N ha⁻¹) than spring (0.35 kg N₂O-N ha⁻¹) applications, and in the spring experiment were significantly lower from cattle slurry than other treatments. Ammonia emissions were generally greater (though not significantly) from spring than autumn applications. Significantly greater NH₃ emissions were measured from layer manure than all other manures at both times of application. N₂O and NH₃ EFs were highly variable depending on the season of application and manure type. The mean autumn and spring N₂O EFs across all manure treatments were 1.72 % and -0.33 % respectively, and mean NH₃ EFs across all treatments were 8.2 % and 15.0 % from autumn and spring applications, respectively. These results demonstrate large deviation from the IPCC default values for N₂O

and NH_3 EFs, and the considerable effect that manure type and time of application have on N_2O and NH_3 emissions.

Keywords: Nitrous oxide, ammonia, livestock manure, agriculture, emission factors.

1 **How do emission rates and emission factors for nitrous oxide and ammonia vary with**
2 **manure type and time of application in a Scottish farmland?**

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19 **1. Introduction**

20 Manures and slurries provide a significant nitrogen (N) input to agricultural land. In 2011
21 the total N excreted by livestock in the EU was 9.2 Tg which is only 15 % less than the N added
22 by synthetic fertilisers (Velthof et al., 2015). The large quantity of nutrients present in manures
23 mean that they are commonly applied to agricultural land to recycle N, phosphorus and
24 potassium for plant growth (Defra, 2010). However, considerable amounts of the applied manure
25 N will not be utilised by crops as a result of nitrification and denitrification, and the subsequent
26 emissions of nitrous oxide (N_2O) (Chadwick et al., 2011), dinitrogen (N_2) (Cardenas et al.,
27 2007), and ammonia (NH_3) (Misselbrook et al., 2005a). Leaching of nitrate (NO_3^-) into
28 groundwater and surface waters leads to further N loss from the soil (Rodhe et al., 2006) and
29 other environmental impacts including eutrophication and soil acidification.

30 Globally, agricultural soil is responsible for 65 % of N_2O emissions (Reay et al., 2012), a
31 greenhouse gas (GHG) approximately 300 times more powerful than CO_2 , that is also
32 responsible for stratospheric ozone layer depletion (Stocker et al., 2013). In the UK it is
33 estimated that 73 % of anthropogenic N_2O emissions and 92 % of NH_3 emissions are from
34 agricultural sources, including direct emissions from soils, animal wastes and manure stores
35 (Dore et al., 2008; Skiba et al., 2012). Indirect N_2O emissions also result from deposition of
36 volatilised NH_3 and NO_3^- leaching and transport in aquatic and terrestrial environments.

37 The potential for N_2O and NH_3 emission after manure applications to agricultural soil is
38 dependent on a combination of manure properties and environmental conditions. High
39 temperatures, high wind speed and low rainfall immediately following manure application
40 promote NH_3 emissions from manures containing a high amount of readily available N
41 (Meisinger and Jokela, 2000; Misselbrook et al., 2005a), meaning that the timing of application

42 can be critical if significant losses of N from the soil are to be avoided. Conversely, loss of N via
43 N₂O emissions is higher when manure is applied in wet conditions as N₂O production via
44 denitrification will occur before the crop is able to utilise the available N. Nitrate leaching will
45 also occur if excess rainfall and drainage take place between manure application and crop N
46 uptake (Defra, 2010; Shepherd and Newell Price, 2013). It is generally recommended therefore
47 to apply manures when crops are actively growing and removing N from the soil (Granli and
48 Bockman, 1994; Meisinger and Jokela, 2000; Defra, 2010).

49 In the UK, manure application in autumn and winter is restricted by Nitrate Vulnerable
50 Zone (NVZ) regulations to decrease NO₃⁻ pollution of aquatic environments. Expansion of these
51 measures to other areas could assist in decreasing indirect N₂O emissions from NO₃⁻ leaching
52 and direct N₂O emissions from denitrification if application in wet conditions is avoided. The
53 time of application should aim to provide a balance between the need to apply manure during the
54 period of maximum crop N requirement, and the need to reduce seasonal climate effects on
55 emissions (Meisinger and Jokela, 2000). Reducing losses of N from the soil is also beneficial for
56 crop growth as more N is available for use by the growing crop (Rodhe et al., 2006; Shepherd,
57 2009).

58 The magnitude of N₂O and NH₃ emissions generated from manures is also dependent on
59 their total-N content and the proportion present as readily available N (ammonium-N and uric
60 acid-N), which varies with manure type (Defra, 2010; Shepherd and Newell-Price, 2013). Large
61 quantities of readily available N (35 - 70 % of total N) are typically found in slurries and poultry
62 manures, compared to only 10 - 25 % of total N in farmyard manure (FYM) (Defra, 2010).
63 Manures containing large amounts of readily available N have a higher probability of losing N
64 via NH₃ volatilization (Misselbrook et al., 2005a), N₂O production (Chadwick et al., 2011), or as

65 a result of NO_3^- leaching (Chambers et al., 2000; Dampney et al., 2000; Shepherd, 2009).
66 Manure moisture content can also affect N_2O emissions, as an increase in soil moisture can
67 enhance the production of N_2O , with greatest N_2O emissions most likely to occur between 50 -
68 70 % WFPS (Flechard et al., 2007). Slurry typically has a moisture content of >90 %, increasing
69 the risk of high N_2O emissions after application (Jorgensen et al., 1998). The moisture content of
70 manures can also affect NH_3 emission rate, and slurries with higher moisture contents are
71 generally associated with lower NH_3 emissions as they rapidly infiltrate into the soil, with the
72 majority of the emission typically occurring in the 12 hours post-application (Sommer and
73 Hutchings, 2001). Poultry litter, in contrast, has a much lower moisture content and a lower
74 initial loss of NH_3 , but emissions occur over a longer timescale as uric acid is broken down and
75 urea hydrolysed to NH_4^+ (Meisinger and Jokela 2000; Jones et al., 2007). It has also been
76 suggested that the C:N ratio of organic manures may affect N losses from soil. Akiyama et al.
77 (2004) argue that higher C:N ratios in manure compared with inorganic chemical fertilisers
78 provide optimum conditions for denitrification. The high C contents of organic manures
79 (typically 35 % organic C), can also stimulate microbial activity, thereby creating anaerobic
80 zones in the soil that allow denitrification and N_2O production to occur at a lower %WFPS than
81 for chemical fertilisers (Akiyama et al., 2004). Incorporation of manures into the soil
82 immediately after application, and the method of slurry application can also influence the extent
83 of N_2O and NH_3 emissions (Webb et al., 2010). However, the use of these methods and their
84 degree of success will depend on the presence/stage of crop growth.

85 The amount of N_2O or NH_3 emitted from N sources applied to soils is often calculated
86 using an emission factor (EF), which defines the quantity of N_2O or NH_3 emitted as a proportion
87 of the total N applied. The UK currently uses the IPCC's Tier 1 EF in its national N_2O inventory,

88 where N₂O emissions from soils receiving organic amendments are equal to 1 % of the total N
89 applied (IPCC, 2006), with no accounting for locally variable factors such as soil type or climate,
90 variations in manure type, or the time of application. The IPCC default EF for NH₃ emission
91 following manure application to land is 20 % of the applied N. However, the EF used to estimate
92 NH₃ emissions from manure application in the UK NH₃ emissions inventory is derived from an
93 empirical model taking account of manure type and some soil and climatic factors (Nicholson et
94 al., 2013).

95 The variety of conditions affecting N loss from soils amended with livestock manures
96 mean it is imperative that applications are carefully managed to avoid significant environmental
97 pollution. It is vital to understand how the form and time of application may affect environmental
98 impacts. The results of the research presented in this paper which forms part of a nationwide
99 project, will contribute to reducing uncertainty in the UK's agricultural GHG inventory, and will
100 enhance the sustainability and GHG mitigation potential of farming systems (GHG, 2013). This
101 study aimed to compare soil N₂O and NH₃ emissions and EFs following autumn and spring
102 manure applications to arable land in Scotland. Nitrous oxide and NH₃ emissions were measured
103 for all manure types following application in both seasons, and the suitability of the IPCC Tier 1
104 EFs to represent N₂O and NH₃ emissions from different manure types and seasons of application
105 was assessed. Effects of the timing and form of manure application on crop yield and crop N
106 uptake were also investigated, to assess the impact of the type and time of manure application on
107 crop production.

108

109 **2. Materials and Methods**

110

111 *2.1. Site description and experimental design*

112 Two 12 month field experiments were undertaken at Boghall farm (NT 248653, 190 m
113 elevation), in East-central Scotland in 2012/2013. Both experiments were located in the same
114 field, on a sandy loam soil (pH 6, 6% OM), with a 30 year (1980-2009) site mean annual
115 precipitation of 979 mm and mean daily temperature in July and January of 14.3 °C and 3.3 °C,
116 respectively. Spring barley (*Hordeum vulgare*) had been grown in the field for the previous four
117 years. The site was one of a network of UK sites measuring emissions as part of the UK GHG
118 research platform, and was selected following a geographical assessment of UK arable land
119 under a range of soil/climatic zones, and a ‘gap analysis’ to identify zones lacking in
120 current/planned experimental data. The entire field, covering both experimental areas was sown
121 with winter wheat (*Triticum aestivum*), a typical crop for the area, on 25th October 2012 at a seed
122 rate of 400 m⁻². In the first experiment manures were applied on 3rd October 2012 to assess N₂O
123 and NH₃ emissions following autumn applications. In the second experiment the crop was left
124 untreated until 10th April 2013, when manures were applied to assess emissions from spring
125 applications. The crop was harvested from both experimental areas on 15th September 2013, with
126 all stubble left in the field and no new crop planted until after the experiment ended. Both
127 experiments ran for a total of 12 months following the date of manure application.

128 Manure treatments (cattle farmyard manure (autumn only), CFYM; broiler litter, BL;
129 layer manure, LM; cattle slurry by trailing hose application, CSTH; cattle slurry by surface
130 broadcast application, CSSB) and a control (to which no manure was added) were applied to a
131 fully replicated randomized block design with three blocks, in each experiment respectively.

132 Treatment plots were orientated in a NNE direction and measured 12 m x 6 m. Manures were
133 applied at rates commonly practiced for the specific manure type, with target application rates
134 for the solid manures of 180 kg total N ha⁻¹, and for slurry of 40 m³ ha⁻¹. In the autumn
135 experiment all manures apart from CFYM were incorporated into the bare soil 24 hours after
136 application, and in the spring experiment they were top dressed on the growing crop. The plots
137 were orientated at 20 degrees to the vertical, and 90 degrees to the prevailing wind to minimise
138 the carry-over of volatilised NH₃ from one plot to another when making NH₃ emission
139 measurements using wind tunnels. Target N application rates and the results of manure chemical
140 analysis were used to calculate total manure application rates. Actual N application rates varied
141 between treatments (Table 1) as a result of changes in the N concentration of the manures
142 between analysis and application, and also due to the rate of manure that would be typically
143 applied in practice for the respective manure types. All manures were sourced from local
144 commercial farms in the autumn, and the un-used quantities were covered to prevent nutrient
145 loss, and stored over-winter on site to enable use of the same materials in the spring experiments,
146 allowing direct comparisons to be made. The slurry was mixed before application and applied in
147 rows at 30 cm spacing using watering cans to simulate trailing hose application. To simulate
148 surface broadcast application the slurry was divided into buckets and splashed evenly across the
149 plots. Solid manures were applied evenly across the plots by hand. Details of treatments are
150 displayed in Table 1. Throughout the experiments plant protection products were applied to meet
151 crop growth requirements, with phosphorus and potassium fertilisers also applied to the plots
152 seven days after spring manure applications.

153

154 *2.2. N₂O and NH₃ emission measurements*

155 Nitrous oxide emission measurements were made using the static chamber method,
156 consistent with the Global Research Alliance guidelines (de Kleine and Harvey, 2012). At the
157 start of each experimental period five square chambers (stackable) made of opaque
158 polypropylene (400 mm x 400 mm x 400 mm, soil surface area coverage of 0.16 m²) were
159 inserted 5cm into the soil on each plot. The chambers remained *in situ* for the entire experiment
160 but were removed when agricultural operations were taking place. Over the course of crop
161 growth, chamber heights were extended using additional stackable chambers to enable sampling
162 to continue. All chambers were stacked at the same time to maintain consistency in the
163 experimental procedure, and the extensions remained in place throughout the growing season.
164 Measurements were made for 12 months for each experiment to determine annual EFs, in
165 compliance with IPCC guidelines. If emission measurements were short of the complete 365 day
166 annual period the flux was extrapolated to 365 days to enable a direct comparison between
167 autumn and spring experiments. Daily gas samples were taken on ten occasions over the first two
168 weeks after manure application, with sampling frequency then reduced to two days a week for
169 the following three weeks. A fortnightly sampling strategy was implemented for the next five
170 months, and reduced to monthly sampling for the remaining six months. The closed static
171 chamber technique described in Chadwick et al. (2014) was used to sample N₂O emissions, with
172 sampling events undertaken between 10 am and 12 noon. On each sampling occasion lids were
173 placed on the chambers and sealed for 40 minutes. After the 40 minute closure period 50ml gas
174 samples were extracted from the chamber lids using a syringe through a valve with a 3-way tap,
175 and transferred to pre-evacuated 20ml glass vials. Ten ambient air samples were taken to
176 represent the concentration of N₂O in the chambers at time zero, and N₂O accumulation within
177 the chambers was assumed to be linear over the 40 minute closure period following a detailed

178 assessment in Chadwick et al. (2014). Following transportation back to the laboratory the N₂O
179 concentration of the gas samples was determined using a gas chromatograph (GC) (Agilent
180 7890A, Berkshire, UK) fitted with an electron capture detector with an N₂O detection limit of
181 0.025 ppmv and a COMBI PAL autosampler (CTC Analytics, Hampshire, UK). GC response
182 was calibrated using certified standard N₂O gas mixtures with N₂O concentrations of 0.35, 1.1,
183 5.1, and 10.7 ppmv. Subtraction of the mean ambient N₂O concentration from the individual
184 chamber N₂O concentrations after 40 minutes, and assumption of linear accumulation of gas
185 within the chamber allowed the change in concentration for each chamber to be calculated.
186 Along with chamber height, the ideal gas law, air temperature and chamber closure time, this
187 data was used to calculate the individual N₂O flux rate for each chamber. The mean flux from
188 each plot (from the five chambers per plot) was then calculated, and used to derive the mean flux
189 and standard error (SE) for each treatment on every sampling occasion. Plot values were used in
190 all statistical analysis, and annual cumulative fluxes were calculated by interpolating the area
191 under the curve between sampling points. A mean cumulative flux and SE was calculated for
192 each treatment using plot means. The use of a large number of chambers per treatment,
193 combined with the intensive N₂O sampling strategy was designed to take into account the high
194 spatial and temporal variability of N₂O emissions from soils, allowing more reliable estimates of
195 N₂O fluxes from each treatment than has been obtained in similar experiments (e.g. Dobbie and
196 Smith, 2003; Smith et al., 2012).

197 Ammonia emissions were measured using small-scale wind tunnels and absorption of
198 NH₃ in orthophosphoric acid (Misselbrook et al., 2005b). The wind tunnels were placed at the
199 top of the plots in the direction of the prevailing wind, and positioned to avoid air entering the
200 tunnel from adjacent treated plots. Each wind tunnel consisted of a transparent polycarbonate

201 canopy (2 m x 0.5 m) which was placed over a section of the plot, with air drawn through the
202 canopy at 1 ms⁻¹ by a fan in a stainless steel duct. Subsamples of the air from the canopy inlet
203 and outlet were passed through absorption flasks containing 80 ml of 0.02 M orthophosphoric
204 acid. On each sampling occasion the flasks of orthophosphoric acid were changed (after 1, 3 and
205 6h on the first day and then daily thereafter) and concentrations of NH₃ in inlet and outlet
206 orthophosphoric acid samples were determined (Misselbrook et al., 2005b). One wind tunnel was
207 placed on each manure treatment plot and NH₃ emissions were measured daily for 7 days from
208 CSSB, CSTH and CFYM, and for 14 days from the LM and BL, accounting for expected
209 differences in the timescales of NH₃ emissions from these treatments (Meisinger and Jokela,
210 2000; Sommer and Hutchings., 2001; Misselbrook et al., 2005a).

211

212 2.3. *Soil Mineral N*

213 The collection of soil samples coincided with N₂O emission measurements, with samples
214 taken weekly in the month following manure application, and once every four to seven weeks for
215 the remaining period. Measurements were made on one representative bulked sample from each
216 plot, consisting of five random samples from the 0 - 10cm soil layer. The samples were sieved (<
217 4 mm) and extracted using 2 M KCl and a soil: extractant ratio of 1:2. Plot average soil
218 ammonium (NH₄⁺-N) and nitrate (NO₃⁻-N) contents were determined by colorimetric analysis
219 (Singh et al. 2011), using a Skalar San⁺⁺ continuous flow autoanalyser (Skalar, York, UK).

220

221 2.4. *Meteorological and additional soil data*

222 A weather station was used to record daily precipitation, and mean and maximum air
223 temperature throughout both experimental periods, with soil temperature (5 cm depth) also
224 measured on each N₂O sampling occasion (RS Components, Northamptonshire, UK). On each
225 N₂O sampling occasion five soil samples (0 - 10 cm depth) were collected from each block and
226 bulked to determine mean block gravimetric moisture content. Metal rings were used to collect
227 and measure soil bulk density before and after ploughing and sowing of the crop in autumn. Soil
228 bulk density values specific to the time of sample collection were then used to convert
229 gravimetric to volumetric moisture contents, and soil water filled pore space (WFPS), assuming
230 a particle density of 2.65 g cm⁻³ (Elliott et al., 1999).

231

232 *2.5. Crop yield and N uptake*

233 Winter wheat from both experiments was harvested on 5th September 2013 using a small
234 plot harvester, with the yield from a dedicated (untouched) 15 m² area recorded for each plot.
235 Additional samples of 100 tillers from each plot were collected by hand to determine the ratio of
236 grain to straw and chaff. The crop yield and the N content and % dry matter (DM) of the grain,
237 straw and chaff was recorded. Grain N content was assumed to be representative of N uptake.

238

239 *2.6. Emission factor calculations*

240 Annual N₂O EFs were calculated by subtracting the cumulative N₂O emission from the
241 control treatment in each block from the cumulative emission from individual treatments in the

242 same block, as in the IPCC methodology, displayed in Equation 1. A mean EF was then
243 calculated for each treatment.

244

EF

$$= \left(\frac{\text{Cumulative } N_2O \text{ flux (kg } N_2O\text{-N)} - \text{cumulative } N_2O \text{ flux from control (kg } N_2O\text{-N)}}{N \text{ applied (kg N)}} \right)$$

× 100

245 Equation 1.

246

247 NH_3 emissions were not measured from the control plots and for the purposes of calculating EFs
248 were assumed to be zero. The calculation of plot mean NH_3 EFs is displayed in Equation 2, with
249 a mean EF then calculated for each treatment.

250

$$EF = \left(\frac{\text{Cumulative } NH_3 \text{ flux (kg } NH_3\text{-N)}}{N \text{ applied (kg N)}} \right) \times 100$$

251 Equation 2.

252

253 2.7. Calculation of indirect N_2O emissions

254 Indirect N_2O emissions from the volatilization of NH_3 and subsequent deposition of
255 NO_3^- or NH_4^+ into terrestrial or aquatic ecosystems were estimated using the assumption that
256 they make up 1 % of the volatilized NH_3 -N (IPCC, 2006). Indirect N_2O emissions associated

257 with N leaching losses were also calculated, assuming that 30 % of applied N is lost via leaching,
258 and 0.75 % of the leached N is re-emitted as N₂O (IPCC, 2006).

259

260 2.8. *Statistical analysis*

261 Statistical analysis was undertaken using GENSTAT (GenStat 16th Edition. Release
262 16.1., VSN International Ltd., Oxford). The data was analysed to assess the impact of manure
263 type and manure application timing on the following variables: annual N₂O emissions, N₂O EFs,
264 annual NH₃ emissions, NH₃ EFs, total N loss as % N applied, annual direct + indirect N₂O
265 emissions, grain yield, grain N uptake, and yield-scaled emissions. Application of CFYM in only
266 the autumn experiment resulted in an un-balanced experimental design, meaning that two
267 separate data analyses were undertaken: one to assess the impact of manure type, and one to
268 assess the impact of manure application timing. In the first analysis the data was split into
269 autumn and spring experiments (with CFYM included in the autumn analysis), and the effect of
270 manure type was investigated for each season separately using a mixed model and the REML
271 (restricted maximum likelihood) algorithm. The random effect model was block and plot nested
272 within block. The effect of treatment was tested using the Wald statistic. In the second analysis
273 the autumn CFYM data was excluded and the effect of season and any season x treatment
274 interactions were investigated. The effect of season, manure type and their interaction was
275 investigated using a mixed model and the REML algorithm. The random effect model was block
276 nested within season, and plot nested within block nested within season. The effect of season,
277 treatment and their interaction was tested using the Wald statistic. For all analysis the data was
278 transformed if necessary to more closely satisfy the assumption that residuals and random effects

279 are normally distributed. The type of transformation varied depending on which gave the better
280 fit when normality of the residuals was analysed. The data were transformed using Box-Cox
281 transformations (Atkinson, 1985), to determine the most suitable value of lambda to use in the
282 transformation (where a lambda of 1 indicates no transformation, 0 = log transformation and 0.5
283 = square root transformation). The equations used in the transformations are shown below Tables
284 2-5 respectively. When data was transformed for statistical analysis both the transformed and
285 back-transformed values are presented in Tables 2-5. The mean and SE for all of the measured
286 variables before data transformation for statistical analysis and removal of outliers are displayed
287 in Supplementary Table 1. Standard error of the difference (SED) values reported in the text are
288 on the transformed scale when data was transformed for analysis. Results were considered
289 statistically significant at $p < 0.05$. If any outliers were identified after the normality of residuals
290 was assessed and these values were considered to be biologically implausible they were removed
291 from the analysis. If biologically plausible and no measurement errors were identified the
292 outliers were retained. The value of -0.90 from control block 1 was removed from analysis of
293 spring annual N_2O and direct + indirect N_2O emissions.

294

295 **3. Results**

296 *3.1. Weather, soil moisture and daily N_2O emissions*

297 As the majority of N_2O emissions are thought to occur in the month immediately
298 following application of an N source to soil (Dobbie et al., 1999), rainfall, temperature and soil
299 moisture during this period were assessed, along with conditions throughout the annual
300 experiments. Approximately twice as much rainfall (172 mm) was measured in the first 30 days

301 of the autumn experiment compared to the spring experiment (82.4 mm), with a maximum daily
302 rainfall of 48.6 mm in the first month of the autumn experiment, compared to only 15.6 mm in
303 the spring experiment (Fig.1). In contrast to the month of application, total rainfall over the
304 respective experimental years was greater in the spring (1388 mm) than the autumn experiment
305 (1178 mm), but this was due largely to high and frequent rainfalls in autumn/winter 2013 (Fig.1
306 b), six months post manure application. Average air temperature in the first 30 days was >1 °C
307 cooler in the autumn experiment (5.6 °C) than the spring (6.8 °C), but on the day of application
308 was higher in autumn (7.7 °C) than spring (1.7 °C) (Fig.1). Average air temperature for the
309 autumn experimental year (7.2 °C) was > 1 °C cooler than the spring experimental year (8.5 °C),
310 due largely to a cold winter in 2012 (Fig.1 a), approximately three months after manure
311 applications. Soil WFPS was closely related to rainfall, with 52 % and 40 % measured on
312 autumn and spring manure application dates, respectively (Fig.1). The large rainfall of 48.6 mm
313 after autumn application, and other further large rainfall events were reflected in an increase in
314 soil WFPS to 59 % on 17th October 2012. Low rainfall in the weeks following spring
315 applications meant that soil WFPS reached a maximum of only 52.1 % on 18th April, falling to
316 very low levels in the summer. This variation in weather and soil conditions between
317 experiments is reflected in the respective experimental N₂O temporal trends and peak emissions.
318 There was a large peak in N₂O from all autumn applications nine days after manure application
319 (Fig.1a), with the greatest emission of 116 g N₂O-N ha⁻¹ d⁻¹ from CSSB on the day when 48.6
320 mm of rainfall was recorded. Nitrous oxide emissions were still high (36 g N₂O-N ha⁻¹ d⁻¹ from
321 CSSB) on 17th October when soil WFPS had reached a maximum. Following spring application
322 N₂O emissions did not demonstrate a single large peak (Fig.1b), with a maximum daily emission

323 of 19.5 g N₂O-N ha⁻¹ d⁻¹ observed from LM on 19th August 2013, after which all N₂O emissions
324 remained below 5 g N₂O-N ha⁻¹ d⁻¹ (Fig. 1b).

325

326 3.2. Soil mineral N and N₂O emissions

327 In the autumn experiment an increase in soil NH₄⁺-N was observed for all manures on the
328 day of application, peaking on 10th October 2012 under LM and BL, whilst decreasing under
329 other treatments. The highest peak of 24 kg NH₄⁺-N ha⁻¹ was measured from BL, and the lowest
330 from CFYM (Fig.2a), reflecting its low readily available N content and lack of soil incorporation
331 (Table 1). Background levels were reached on 26th October 2012. Soil NO₃⁻-N contents also
332 increased after autumn applications, reached a peak between 3rd and 10th October, dropped to
333 lower levels by 16th October, and reached background levels by 3rd December 2012 (Fig.2b). The
334 largest peak of 107 kg NO₃⁻-N ha⁻¹ was measured from the manure with the highest NH₄⁺-N
335 content available for nitrification, LM (Table 1) on 10th October 2012. The decrease in soil NO₃⁻
336 -N between 10th and 16th October corresponded to the N₂O emission peak on 12th October
337 (Fig.2c), reflecting a process of denitrification, at a time of high rainfall and increasing WFPS
338 (Fig.1a). A decrease in soil NO₃⁻-N from all treatments between 8th November 2012 and 3rd
339 December 2012 corresponded with a small N₂O emission peak on 19th November (Fig.2 b,c),
340 indicating further denitrification.

341 Although there was a small peak following spring manure applications, soil NH₄⁺-N was
342 lower than in the autumn experiment, and the greatest peak of 19 kg NH₄⁺-N ha⁻¹ was measured
343 from LM 33 days after manure application (Fig.2d). Soil NO₃⁻-N peaked between 12th April
344 2013 and 13th May 2013, but was also much lower than in the autumn experiment, with a peak of

345 57 kg N ha⁻¹ from LM 33 days after application (Fig.2e). Further small peaks in NH₄⁺-N and
346 NO₃⁻-N were measured between 29th July 2013 and 19th August 2013, before decreasing to <5 kg
347 N ha⁻¹ for the remainder of the experiment. Small peaks in soil mineral N relative to the autumn
348 experiment correspond with much smaller peaks in N₂O (Fig.2f), and also to greater losses of
349 NH₃ in the spring experiment (Fig.3). Small peaks in N₂O immediately after manure application
350 and on 19th August correspond to increases in soil NO₃⁻-N; however N₂O peaks on 26th June and
351 29th July correspond with decreasing levels of soil NO₃⁻-N, indicative of both nitrification and
352 denitrification.

353

354 3.3. Ammonia emissions

355 Emissions of NH₃ following autumn manure applications were greatest in the first hour
356 for all manures apart from BL, which had slightly higher emissions three hours after application.
357 The greatest emission rate of 2.8 kg NH₃-N ha⁻¹ hr⁻¹ was measured from LM when emissions
358 from CSSB were also high (1.1 kg NH₃-N ha⁻¹ hr⁻¹). Emissions from all other manures were <
359 0.4 kg NH₃-N ha⁻¹ hr⁻¹ in the first hour after application, and other than the small increase to 0.5
360 kg NH₃-N ha⁻¹ hr⁻¹ from BL three hours after application, remained low throughout the
361 measurement period. Emissions from LM remained > 1 kg NH₃-N ha⁻¹ hr⁻¹ until six hours after
362 application, fell to < 0.2 kg NH₃-N ha⁻¹ hr⁻¹ 48 hours after application, but remained higher than
363 all other manures for the whole experiment (Fig. 3a). Emissions in the first hour after spring
364 applications were also highest from LM (1.6 kg NH₃-N ha⁻¹ hr⁻¹), but were lower than in the
365 autumn experiment. In contrast to the autumn experiment, emission rates from LM, BL and
366 CSSB increased in the first few hours after application, with greatest emissions of 2.7 kg NH₃-N

367 $\text{ha}^{-1} \text{hr}^{-1}$ six hours after application from LM. Emissions from all manures declined to $< 0.4 \text{ kg}$
368 $\text{NH}_3\text{-N ha}^{-1} \text{hr}^{-1}$ 24 hours after application, with a small increase from LM 72 hours after
369 application (Fig.3b). Although rainfall was much greater over the 14 day measurement period in
370 autumn (83.8 mm) than spring (42.4 mm), the two measurement periods experienced very
371 similar mean air temperatures of $6.2 \text{ }^\circ\text{C}$ and $6.5 \text{ }^\circ\text{C}$, respectively.

372

373 *3.4 Annual N₂O fluxes and EFs*

374 *3.4.1. Manure type*

375 Annual N₂O emissions from the autumn experiment ranged from $0.63 \text{ kg N}_2\text{O-N ha}^{-1}$
376 from the control to $2.48 \text{ kg N}_2\text{O-N ha}^{-1}$ from LM (Table 2), but there were no significant
377 differences between any treatments ($p = 0.083$; standard error of the difference (SED) = 0.56). A
378 significant difference between treatments was however observed in the spring experiment ($p =$
379 <0.001 ; SED = 0.11), with significantly lower emissions from CSSB and CSTH than all other
380 treatments (Table 2). Annual N₂O EFs for autumn manure applications ranged from 0.27 % for
381 CFYM to 2.17 % for CSSB, with significant differences between treatments ($p = 0.007$; SED =
382 0.43) (Table 2). The EFs displayed large variation around the IPCC default value of 1 %. In the
383 spring experiment EFs ranged from -1.07 % for CSTH to 0.34 % for BL, but high variability
384 within treatments meant there were no significant differences ($p = 0.408$; SED = 0.83). All of the
385 EFs for spring manure applications were well below the IPCC default of 1 %. The negative EFs
386 measured from CSTH and CSSB in the spring experiment were a consequence of emissions
387 from manure applications often being as small as, or smaller than, emissions from the control. In

388 the spring experiment large variation within EFs was observed when high/low emissions from
389 control plots occurred in the same block as low/high emissions from slurry treatments.

390

391 *3.4.2. Timing of application*

392 The mean annual N₂O emission from all autumn treatments (2 kg N₂O-N ha⁻¹) was
393 significantly different to that from spring treatments (0.35 kg N₂O-N ha⁻¹) (p = 0.004; SED =
394 0.27). There was no significant season x treatment interaction, indicating that emissions from all
395 manures were significantly greater when applied in autumn than spring (Table 3). There was no
396 significant difference between the mean EFs for autumn and spring applications (p = 0.145; SED
397 = 0.99) (Table 3).

398

399 3.5. Annual NH₃ fluxes and EFs

400 *3.5.1. Manure type*

401 Cumulative NH₃ emissions in the autumn experiment ranged from 0.7 kg NH₃-N ha⁻¹ for
402 CFYM to 39.2 kg NH₃-N ha⁻¹ for LM, with a significant difference between treatments (p =
403 <0.001; SED = 1.73) (Table 2). In the spring experiment, cumulative NH₃ emissions ranged
404 from 5.19 kg NH₃-N ha⁻¹ from CSTH to 36.4 kg NH₃-N ha⁻¹ from LM, and again there was a
405 significant difference between treatments (p=0.04; SED=0.53) (Table 2). Annual NH₃ EFs for
406 manures applied in autumn were significantly different between treatments (p = < 0.001; SED =
407 0.67) (Table 2), and ranged from 0.3 % for CFYM to 16.0 % for LM. Autumn EFs were all much
408 lower than the IPCC default of 20 %. In the spring experiment there were no significant

409 differences in NH₃ EFs between manures ($p = 0.570$; $SED = 1.73$) (Table 2), and all of the EFs
410 were below the IPCC default value of 20 %.

411

412 *3.5.2. Timing of application*

413 The only manure with significantly different NH₃ emissions between seasonal
414 experiments was BL, with 17.9 kg NH₃-N ha⁻¹ emitted following spring applications, and 3.6 kg
415 NH₃-N ha⁻¹ following autumn applications (Table 3). Although the NH₃ EFs were generally
416 greater from spring than from autumn applications, there were no statistically significant
417 differences between seasons ($p = 0.06$; $SED = 0.98$) (Table 3).

418

419 3.6. Total N (NH₃-N + N₂O-N) loss as % N applied

420 *3.6.1. Manure type*

421 In the autumn experiment there was a significant difference in total N loss as a % of N
422 applied between treatments ($p = <0.001$; $SED = 0.272$), with the greatest emission of 17.1 % N
423 applied from LM, and the lowest of 1.1 % of N applied from CFYM. Total N loss as % N
424 applied was significantly greater from BL than CFYM, but significantly less than from CSSB
425 and CSTH (Table 2). There was no difference between the two slurry treatments (i.e. no effect of
426 application method). Manure type had no significant impact on total N loss as a % of N applied
427 in the spring experiment ($p = 0.56$, $SED = 2.24$).

428

429 3.6.2. *Timing of application*

430 There were no statistically significant differences between seasons of manure application
431 ($p = 0.15$; $SED = 2.37$), and no significant season x treatment interaction ($p = 0.16$; $SED = 4.10$)
432 (Table 3).

433

434 3.7. Direct + Indirect N₂O emissions

435 3.7.1. *Manure type*

436 There was a significant difference between treatments following autumn ($p = 0.02$; SED
437 $= 0.527$) and spring ($p = <0.001$; $SED = 0.09$) applications. In the autumn experiment greatest
438 emissions were measured from LM (3.45 kg N₂O-N ha⁻¹) and lowest from the control (Table 2).
439 Following spring applications emissions from LM (1.68 kg N₂O-N ha⁻¹) were significantly
440 greater than all treatments apart from BL (Table 2). Lowest emissions were measured from
441 CSTH (0.03 kg N₂O-N ha⁻¹) but these were not significantly different to those from CSSB.

442

443 3.7.2. *Timing of application*

444 Mean emissions from all manure treatments were significantly greater in the autumn
445 experiment (2.34 kg N₂O-N ha⁻¹) than the spring experiment (0.69 kg N₂O-N ha⁻¹) ($p = 0.004$;
446 $SED = 0.27$). This difference between seasons was evident for all types of manure (Table 3).

447

448 3.8. Wheat grain yield, yield-scaled emissions and N uptake

449 3.8.1. *Manure type*

450 Grain yields were lower than would usually be expected due to delayed crop sowing
451 caused by unsuitable weather conditions and crop damage from birds. There was a significant
452 difference in grain yields produced from different manures in the autumn ($p = 0.02$; $SED = 0.31$)
453 and spring ($p = 0.01$; $SED = 0.32$) experiments (Table 4). In the autumn experiment maximum
454 grain yield (3.48 t ha^{-1}) was produced from BL, and the lowest yield from the control. In the
455 spring experiment maximum yield was produced from LM (5.05 t ha^{-1}) and minimum yield from
456 the control. Yield-scaled emissions from manures applied in autumn ranged from $0.29 \text{ kg N}_2\text{O-N}$
457 $+ \text{NH}_3\text{-N t}^{-1}$ grain for the control to $14.45 \text{ kg N}_2\text{O-N} + \text{NH}_3\text{-N t}^{-1}$ grain from LM. In the spring
458 experiment these ranged from $0.33 \text{ kg N}_2\text{O-N} + \text{NH}_3\text{-N t}^{-1}$ grain from the control to 7.42 kg
459 $\text{N}_2\text{O-N} + \text{NH}_3\text{-N t}^{-1}$ grain from LM. A significant difference between treatments was observed in
460 both the autumn ($p = <0.001$; $SED = 0.49$) and spring ($p = <0.001$; $SED = 0.45$) experiments
461 (Table 4). There was a significant difference in grain N uptake between manures when applied in
462 autumn ($p = 0.014$; $SED = 4.70$) and spring ($p = 0.013$; $SED = 9.67$). In the autumn experiment,
463 this ranged from $31.9 \text{ kg N ha}^{-1}$ for the control to $49.7 \text{ kg N ha}^{-1}$ for CFYM (Table 4). In the
464 spring experiment grain N uptake from LM ($70.6 \text{ kg N ha}^{-1}$) was significantly greater than from
465 all other treatments. Grain N uptake from LM and CSSB was significantly greater than from the
466 control ($22.7 \text{ kg N ha}^{-1}$) (Table 4).

467

468 3.8.2. *Timing of application*

469 For the grain yields, there was a significant season x treatment interaction ($p = 0.01$; SED
470 $= 0.23$) (Table 5), with only LM producing a significantly higher yield following spring (5.04 t
471 ha^{-1}) compared to autumn (2.91 t ha^{-1}) application. In terms of the yield-scaled emissions, there

472 was also a significant interaction between season and treatment ($p = <0.001$; $SED = 0.84$), being
473 significantly greater in the autumn experiment than the spring experiment for LM, but
474 significantly lower in the autumn experiment than the spring experiment for BL (Table 5).
475 There was also a significant season x treatment interaction for grain N uptake ($p = 0.015$; $SED =$
476 0.42) (Table 5), with only LM producing significantly greater grain N uptake from spring than
477 autumn applications.

478

479 **4. Discussion**

480 *4.1. Timing of application*

481 Wetter conditions observed in the month of autumn applications compared to spring
482 applications in this study reflects 30 year long-term average seasonal differences (78.3 mm:
483 October; 42.5 mm: April), and suggests that livestock manure should be applied in spring if
484 production of N_2O is to be minimised. The observed relationship between N_2O emissions, large
485 rainfall events and increasing soil WFPS does though emphasise that it is the short-term weather
486 after application that is the strongest driver in generating these emissions, and therefore any
487 deviation from seasonal trends may mean that recommendations should be based on weather
488 conditions rather than time of year. As greatest N_2O emissions are expected between a WFPS of
489 50-70% when denitrification is the dominant N_2O producing process (Davidson, 1991; Dobbie et
490 al., 1999), the higher soil WFPS measured after autumn applications in this study is likely to
491 have promoted greater N_2O emissions when large amounts of NH_4^+ and C were available
492 (Clemens and Huschka, 2001). Although the rainfall in these experiments reflects the long-term
493 seasonal trend of greater precipitation in October than April, the magnitude of rainfall that fell in

494 both months was greater than the long-term average, making it is possible that the N₂O
495 emissions measured here will be larger than those generated in more representative years, a
496 limitation of this one year study. The suggestion to apply manures in drier conditions based on
497 the evidence presented in this study is supported by the reduction in NO₃⁻ leaching that would
498 also result, with autumn application to agricultural land already restricted in many areas of the
499 UK by NVZ requirements (Defra, 2013; The Scottish Government, 2014). It could be argued that
500 regulations should be more widespread to limit large N₂O emissions outside the NVZ; however
501 enforcement may be controversial due to a lack of required overwinter manure and slurry storage
502 areas (FAS, 2013).

503 In contrast to N₂O, where soil and weather conditions in the weeks preceding and
504 following manure application may influence emissions, NH₃ emissions are much more
505 influenced by soil and weather conditions on the day of application. Wind speed and DM content
506 have been identified as important influencing factors in generating NH₃ emissions from slurry
507 (Sommer et al., 2003; Misselbrook et al., 2005a), as well as the soil surface conditions which
508 influence the rate of infiltration (Sommer et al., 2003; Misselbrook et al., 2005c). For solid
509 manures, rainfall after application is the most important factor, although the effect can vary
510 depending on timing, duration and intensity (Misselbrook et al., 2005a). Rainfall during the first
511 48 hours after application in the present study was very low for both experiments (4.2 mm in
512 autumn and 0.8 mm in spring). Air temperature has often demonstrated a strong influence on
513 emissions (Sommer and Olesen, 1991; Meisinger and Jokela, 2000), and although the two
514 experiments had similar mean air temperatures over the 14 days of measurement, the temperature
515 in the 48 hours after applications was much lower in spring (2.1°C) than autumn (7.6 °C) (Fig.1).
516 The fact that air temperature did not exceed 8 °C at the time of application in either experiment

517 could help explain the lack of significant differences between experiments. Wind speed and
518 humidity were not measured in these experiments, but are variables that could also play an
519 important role (Brunke et al., 1988). This study has shown that it is very short-term weather
520 conditions that have the biggest control on NH_3 emissions, suggesting that decisions regarding
521 the timing of application should perhaps be dictated by short-term weather rather than calendar
522 season. These results also demonstrate the requirement to consider both forms of gaseous N loss
523 in decisions regarding when to apply livestock manures, and the importance of including NH_3
524 measurements in addition to N_2O . When emissions from both experiments are compared as a %
525 of the N applied (Table 3), the significantly greater direct and indirect N_2O emissions from
526 autumn applications are counteracted by greater NH_3 emissions in spring.

527 Incorporation of the manures into the soil in the autumn experiment, compared to top-
528 dressing in the spring could also help to explain higher annual N_2O emissions from autumn
529 applications. This will have provided soil microorganisms rapid access to manure N and
530 increased soil moisture, both of which promote N_2O production. Manures applied in spring
531 remained on the soil surface for longer, and would be less accessible to soil microorganisms
532 (Wulf et al., 2001; Velthof et al., 2003; Perala et al., 2006; Rodhe et al., 2006) and more prone to
533 NH_3 volatilisation, supported by the lower soil $\text{NH}_4^+\text{-N}$ levels measured in spring. Although
534 NH_3 emissions were generally higher from manures applied in spring, BL was the only treatment
535 to show a significant difference. This could be explained by the higher readily available N
536 content (Table 1) of the BL applied in spring (Defra, 2010); however this would also have been
537 expected to increase N_2O emissions. The significantly greater NH_3 emissions in the spring are
538 unlikely to be the result of top-dressing the spring applications, as the manures were not
539 incorporated into the soil in the autumn experiment until 24 hours after application, by which

540 time NH₃ emissions had already declined to very low levels (Fig.3). To be an effective
541 mitigation method soil incorporation should therefore be undertaken very soon after application.

542 Although the application of manures to bare soil in the autumn experiment generated
543 greater losses of N₂O than when manures were applied to a growing crop in the spring
544 experiment, higher grain N uptake in the spring experiment compared to the autumn experiment
545 was only measured for LM. Higher N uptake, as demonstrated by Limaux et al. (1999), did not
546 occur under the other manures and it is unlikely therefore, that crop N uptake influenced N₂O or
547 NH₃ emissions. The general lack of difference in crop yield between autumn and spring
548 experiments, combined with generally greater N₂O emissions after autumn application and
549 greater NH₃ emissions after spring application produced similar yield-scaled emissions for most
550 autumn and spring applications. Season of manure application thus had no effect on the amount
551 of emissions per unit of yield obtained.

552

553 *4.2. Manure type:*

554 Although annual N₂O emissions did not differ significantly between any of the manures
555 applied in the autumn experiment, it must be realised that the total N applied varied between
556 manures (Table 1). It is possible that high N₂O emissions from cattle slurry with a low N
557 application rate could be the result of its low DM content (Table 1), which may have increased
558 soil moisture and N₂O production by denitrification (Davidson, 1992). Although soil WFPS
559 remained below the denitrification “threshold” of 60%, localised hotspots (WFPS >60%) are
560 likely to have occurred within the soil volume. Significantly lower emissions from CSSB and
561 CSTH than from the other manures in the spring experiment does though suggest that applying

562 manures with a lower N content can reduce N₂O emissions. Comparison of N₂O EFs takes N
563 application rate into account, and the lack of a significant difference between spring EFs, and a
564 significant difference between autumn EFs reflects the annual N₂O emission results.

565 In relation to NH₃, the significantly greater cumulative emissions measured from LM
566 than all other manures in both experiments can be explained not only by higher peak emissions,
567 but also by the longer timescale over which emissions occurred (Fig.3). This is thought to result
568 from the high N application rate and NH₄⁺-N content of LM promoting NH₃ production, along
569 with the slow breakdown of uric acid and conversion to urea, followed by urea hydrolysis to
570 ammonium (Misselbrook et al., 2000; Sommer and Hutchings, 2001). Manures with a low DM
571 content also infiltrate faster into the soil (Menzi et al., 1997; Chambers et al., 1999) which could
572 explain the smaller losses of NH₃ from the high moisture content slurries compared to the solid
573 manures. The lack of any significant differences in N₂O and NH₃ emissions between CSSB and
574 CSTH demonstrates that method of slurry application had no effect on either flux, in contrast to
575 research where 30-70% lower NH₃ emissions were measured from CSTH than CSSB (Pain and
576 Misselbrook, 1997; Webb et al., 2010). The low DM content of the cattle slurry used in this
577 experiment may have reduced the effectiveness of the CSTH treatment in lowering NH₃
578 emissions, as slurry DM content can influence the degree to which it remains in bands after
579 trailing hose application, and therefore the extent to which the emitting surface area is
580 minimised. Additionally, trailing hose application is more effective in reducing NH₃ emissions
581 when a crop canopy is present (Thorman et al., 2008), which was not the case for the autumn
582 application. Similarly, although the crop was established at the time of spring application, there
583 had been very little canopy development.

584 The impact of manure type on grain yield and N uptake was evident in the spring
585 experiment, where the highest grain yield and N uptake were measured in winter wheat treated
586 with LM. This manure had the highest NH_4^+ -N content and N application rate in both
587 experiments; however the higher yield and N uptake were not observed following autumn
588 applications. This was most likely due to the much greater loss of NH_3 from LM applications
589 relative to other fertilisers in autumn, leading to less N being available for crop uptake. The
590 lowest yield-scaled emissions in the autumn experiment measured from CFYM and BL indicate
591 that these manures generate the lowest N_2O and NH_3 emissions whilst maximising grain yield,
592 but the lowest yield-scaled emissions measured in the spring experiment from CSSB and CSTH
593 emphasise the variation caused by time of manure application. Layer manure did however
594 produce the highest yield-scaled emissions at both times of application.

595

596 *4.3. Comparison to previously reported EFs and the IPCC default EFs*

597 The large variation in EFs reported in this study from different types of livestock manure,
598 and from the same type of manure applied at different times (Table 3), supports the findings of
599 previous research. Nitrous oxide EFs for CSSB of 2.57% when applied in autumn, and - 0.90%
600 when applied in spring, demonstrate considerable variation in EFs for the same manure
601 depending on the timing of application. This adds support to the large variation in EFs reported
602 for dairy cow slurry in Chadwick et al. (2000) and Velthof and Mosquera (2011), ranging from
603 0.12% to 0.97%. The high variability in N_2O EFs measured in this study means they are neither
604 consistently higher nor lower than those reported elsewhere. Autumn and spring LM EFs of 0.77
605 % and 0.20 %, respectively, are much smaller than the 2.40 % reported in Webb et al. (2014),

606 compared to autumn and spring BL EFs of 1.08 % and 0.36 % respectively, which are much
607 greater than the 0.05 % reported in Chadwick et al. (2000). The EF of 0.27% measured in this
608 study for CFYM is in the range (0.09% - 0.55%) reported from two English sites in Webb et al.
609 (2014). The identification of large variation in EFs, both within this study and within the
610 literature, suggests that environmental variables, soil type, soil conditions and manure properties
611 can have a large impact on emissions. There is a clear requirement for EFs to account for these
612 environmental and soil variables, and to account for the type of manure applied. The mean EF of
613 1.72 % for autumn manure applications is larger than the IPCC default of 1 %, suggesting that
614 the recently adjusted value of 1.25 % (IPCC, 2006) was perhaps more appropriate, however the
615 mean EF of - 0.33 % from spring applications is much lower than the 1 % default. This research
616 demonstrates that weather conditions following autumn and spring applications could be
617 markedly different, making it inappropriate to use a single EF value for all types of manure and
618 periods of application.

619 NH_3 EFs measured in this study were also highly variable and often higher than those
620 reported in the literature, but lower than the IPCC default value of 20 %. Surface spreading of
621 cattle slurry produced EFs ranging from 8.2 % - 18.6 %, greater than the 6 - 12 % reported in
622 Van der Hoek (1998), and LM EFs of 16 % reported here are much larger than the 0.15 % and 7
623 % reported in Van der Hoek (1998) and Sommer and Hutchings (2001) respectively. All of the
624 NH_3 EFs measured in this study from both seasons of application were lower than the IPCC
625 default value of 20 %, despite the different weather conditions. This suggests that use of the
626 default IPCC EF could overestimate NH_3 emissions from manures applied under these
627 environmental conditions, and that using country-specific EFs for manure applications in the UK
628 NH_3 emission inventory may be more appropriate.

629

630 **5. Conclusion**

631 The results of this research demonstrate how manure type and the time of its application
632 can influence N₂O and NH₃ emissions, and that the trade-off between N₂O and NH₃ emissions
633 could be crucial in deciding on timing and method of application for different manure types. The
634 variation in the extent of emissions from different types of manure demonstrates the effects of
635 manure properties such as moisture content, total N and available N content on emission
636 generation. Emissions of N₂O were strongly affected by the timing of manure application,
637 reflecting the effects of weather conditions, manure incorporation and crop growth on production
638 of N₂O, with greatest N₂O emissions measured from manures applied and incorporated into bare
639 soil in warmer and wetter autumn conditions. Although not significantly different between
640 seasons, emissions of NH₃ were conversely greater from manures applied in spring. Crop yield
641 was generally unaffected by manure application timing or manure type, but yield scaled
642 emissions were significantly greater from LM than all other manure types. There was high
643 variability in N₂O and NH₃ EFs, dependent on manure type and application timing, and large
644 deviation from the IPCC default EF values for N₂O and NH₃ emissions. This highlights the
645 requirement for N₂O and NH₃ EFs to take into account the effect of manure type and timing of
646 application in order to improve the accuracy of national inventories of N₂O and NH₃ emission.
647 Future research is needed to determine whether the results obtained from this work are applicable
648 to different geographical areas, and to take into account the loss of N via leaching.

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657

658 **References**

659 Akiyama, H., McTaggart, I., Ball, B., Scott, A., 2004. N₂O, NO and NH₃ emissions from soil
660 after the application of organic fertilisers, urea and water. *Water, Air, and Soil Pollution* 156,
661 113–129.

662

663 Atkinson, A.C., 1985. *Plots, Transformations and Regression*. Oxford University Press, Oxford.

664

665 Brunke, R.P., Alvo, P., Schuepp, P., Gordon, R., 1988. Effect of meteorological parameters on
666 ammonia loss from manure in the field. *Journal of Environmental Quality* 17, 431-436.

667

668 Cardenas, L.M., Chadwick, D., Scholefield, D., Fychan, R., Marley, C.L., Jones, R., Bol, R.,
669 Well, R., Vallejo, A., 2007. The effect of diet manipulation on nitrous oxide and methane

670 emissions from manure application to incubated grassland soils. *Atmospheric Environment* 41,
671 7096-7107.

672

673 Chadwick, D., Pain, S., Brookman, S., 2000. Nitrous Oxide and Methane Emissions following
674 Application of Animal Manures to Grassland. *Journal of Environmental Quality* 29, 277-287.

675

676 Chadwick, D., Sommer, S., Thorman, R., Fangueiro, D., Cardenas, L., Amon, B., Misselbrook,
677 T., 2011. Manure management: Implications for greenhouse gas emissions. *Animal Feed Science*
678 *and Technology* 166-167, 514-531.

679

680 Chadwick D., Cardenas L.M., Misselbrook T., Smith K.A., Rees R.M., Watson C., McGeough,
681 K.L., Williams J., Cloy J.M., Thorman R., Dhanoa D., 2014. Optimizing chamber methods for
682 measuring nitrous oxide emissions from plot-based agricultural experiments. *European Journal*
683 *of Soil Science* 65, 295-307.

684

685 Chambers, B., Lord, E., Nicholson, F., Smith., K., 1999. Predicting nitrogen availability and
686 losses following application of organic manures to arable land: MANNER. *Soil Use and*
687 *Management* 15, 137-143.

688

689 Chambers, B.J., Smith, K.A., Pain, B.F., 2000. Strategies to encourage better use of nitrogen in
690 animal manures. *Soil Use and Management* 16, 157-161.

691

692 Clemens, J., Huschka, A., 2001. The effect of biological oxygen demand of cattle slurry and soil
693 moisture on nitrous oxide emissions. *Nutrient Cycling in Agroecosystems* 59, 193–198.

694

695 Dampney, P.M.R, Lord, E.I., Chambers, B.J., 2000. Development of improved advice for
696 farmers and advisers. *Soil Use and Management* 16, 162-166.

697

698 Davidson, E., 1991. Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In:
699 Rogers, J.E., Whitman, W.B. (Eds), *Microbial Production and Consumption of Greenhouse*
700 *Gases: Methane, Nitrogen Oxides and Halomethanes*, American Society of Microbiology,
701 Washington, pp. 219-235.

702

703 Davidson, E., 1992. Sources of nitric-oxide and nitrous oxide following wetting of dry soil. *Soil*
704 *Science Society of America Journal* 56, 95-102.

705

706 De Kleine, C.A.M, Harvey, M.J., 2012. Nitrous oxide chamber methodology guidelines. Global
707 Research Alliance. Ministry of Primary Industries, New Zealand, pp 1-146. Available

708 via: www.globalresearchalliance.org/research/livestock/activities/nitrous---oxide---chamber---methodology---guidelines/

710

711 Defra., 2010. The Fertiliser Manual (RB209). 8th edition. TSO, Norwich, pp 1-249.

712

713 Defra., 2013. Guidance on complying with the rules for Nitrate Vulnerable Zones in England for
714 2013 to 2016. <https://www.gov.uk/nitrate-vulnerable-zones>. Accessed 17/06/2015.

715

716 Dobbie, K.E., McTaggart, I.P., Smith, K.A., 1999. Nitrous oxide emissions from intensive
717 agricultural systems: variations between crops and seasons, key driving variables, and mean
718 emission factors. *Journal of Geophysical Research-Atmospheres* 104, 26981- 26899.

719

720 Dobbie, K.E., Smith, KA., 2003. Nitrous oxide emission factors for agricultural soil in Great
721 Britain: the impact of soil water-filled pore space and other controlling variables. *Global Change*
722 *Biology* 9, 204–218.

723

724 Dore, C., Murrels, T., Passant, N., Hobson, M., Thistlethwaite, G., Wagner, A., Li, Y., Bush, T.,
725 King, K., Norris, J., Coleman, P., Walker, C., Stewart, R., Tsagatakis, I., Conolly, C., Brophy,
726 N., Hann, M., 2008. *UK Emissions of Air Pollutants 1970 to 2006*. Didcot, Oxford, UK, pp. 1-
727 170.

728

729 Elliott, E.T., Heil, J.W., Kelly, E.F., Monger, H.C., 1999. Soil Structural and Other Physical
730 Properties. In: Robertson, G.P., Bledsoe, C.S., Coleman, D.C., Sollins, P. (Eds), Standard Soil
731 Methods for Long-Term Ecological Research, Oxford University Press, Oxford, pp. 74-85.

732

733 FAS, 2013. FAS technical article- slurry storage requirements. Available
734 from: <http://farmingadvice.service.org.uk/events/newsletters/>, accessed 17/06/2015.

735

736 Flechard, C.R., Ambus, P., Skiba, U., Rees, R.M., Hensen, A., van Amstel, A., Pol-van
737 Dasselaar, A.V., Soussana, J.F., Jones, M., Clifton-Brown, J., Raschi, A., Horvath, L., Neftel, A.,
738 Jocher, M., Ammann, C., Leifeld, J., Fuhrer, J., Calanca, P., Thalman, E., Pilegaard, K., Di Marco, C.,
739 Campbell, C., Nemitz, E., Hargreaves, K.J., Levy, P.E., Ball, B.C., Jones, S.K., van de
740 Bulk, W.C.M., Groot, T., Blom, M., Domingues, R., Kasper, G., Allard, V., Ceschia, E., Cellier, P.,
741 Laville, P., Henault, C., Bizouard, F., Abdalla, M., Williams, M., Baronti, S., Berretti, F., Grosz, B.,
742 2007. Effects of climate and management intensity on nitrous oxide emissions in grassland
743 systems across Europe. Agriculture Ecosystems & Environment 121, 135-152.

744

745 GHG, 2013. www.ghgplatform.org.uk

746

747 Granli, T., Bøckman, O.C., 1994. Nitrous oxide from agriculture. Norwegian Journal of
748 Agricultural Science 12, 7–128.

749

750 IPCC, 2006. In: Eggleston, H.S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (Eds.), 2006
751 IPCC Guidelines for National Greenhouse Gas Inventories. IGES, Hayama, Japan Prepared by
752 the National Greenhouse Gas Inventories Programme.

753

754 Jørgensen, R., Jørgensen, B., Nielsen, N., 1998. N₂O emission immediately after rainfall in a dry
755 stuble field. Soil Biology and Biochemistry 30, 545-546.

756

757 Jones, S., Rees, R., Skiba, U., Ball, B., 2007. Influence of organic and mineral N fertiliser on
758 N₂O fluxes from a temperate grassland. Agriculture, Ecosystems & Environment 121, 74-83.

759

760 Limaux, F., Recoux, S., Meynard, J-M., Guckert, A., 1999. Relationship between rate of crop
761 growth at date of fertiliser N application and fate of fertiliser N applied to winter wheat. Plant
762 and Soil 214, 49-59.

763

764 Meisinger, J., Jokela, W., 2000. Ammonia volatilization from dairy and poultry manure.
765 Managing nutrients and pathogens from animal agriculture. Proceedings of a Conference for

766 Nutrient Management Consultants, Extension Educators, and Producer Advisors, Camp Hill,
767 Pennsylvania, March 28-30, 2000.

768

769 Menzi, H., Katz, P., Frick, R., Fahrni, M., Keller, M., 1997. Ammonia emissions following the
770 application of solid manure to grassland. In: Jarvis, S., Pain, B. (Eds), Gaseous nitrogen
771 emissions from grassland. CAB International, Wallingford, pp 265-274.

772

773 Misselbrook, T.H., Van der Weerden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J., Smith, K.A.,
774 Philips, V.R., Demmers, T.G.M., 2000. Ammonia emission factors for UK agriculture.
775 Atmospheric Environment 34, 871-880.

776

777 Misselbrook, T.H., Nicholson, F.A., Chambers, B.J., 2005a. Predicting ammonia losses following
778 the application of livestock manure to land. Bioresource Technology 96, 159-168.

779

780 Misselbrook, T., Nicholson, F., Chambers, B., Johnson, R., 2005b. Measuring ammonia
781 emissions from land applied manure: an intercomparison of commonly used samplers and
782 techniques. Environmental Pollution 135, 389-397.

783

784 Misselbrook, T.H., Scholefield, D., Parkinson, R., 2005c. Using time domain reflectometry to
785 characterize cattle and pig slurry infiltration into soil. Soil Use and Management 21, 167-172.

786

787 Nicholson, F. A., Bhogal, A., Chadwick, D., Gill, E., Gooday, R.D., Lord, E., Misselbrook, T.,
788 Rollett, A.J., Sagoo, E., Smith, K.A., Thorman, R.E., Williams, J.R., Chambers, B.J., 2013. An
789 enhanced software tool to support better use of manure nutrients: MANNER-NPK. *Soil Use and*
790 *Management* 29, 473-484.

791

792 Pain, B., Misselbrook, T., 1997. Sources of variation in ammonia emission factors for manure
793 applications to grassland. In: Jarvis, S., Pain, B. (Eds), *Gaseous nitrogen emissions from*
794 *grassland*. CAB International, Wallingford, pp 293-301.

795

796 Perala, P., Kapuinen, P., Esala, M., Tyynela, S., Regina, K., 2006. Influence of slurry and
797 mineral fertiliser application techniques on N₂O and CH₄ fluxes from a barley field in southern
798 Finland. *Agriculture, Ecosystems and Environment* 117, 71–78.

799

800 Reay, D.S, Davidson, E.A., Smith, K.A., Smith, P., Melillo, J.M., Dentener, F., Crutzen, P.J.,
801 2012. Global agriculture and nitrous oxide emissions. *Nature Climate Change* 2, 410-416.

802

803 Rodhe, L., Pell, M., Yamulki, S., 2006. Nitrous oxide, methane and ammonia emissions
804 following slurry spreading on grassland. *Soil Use and Management* 22, 229-237.

805

806 Shepherd, T.G., 2009. Visual Soil Assessment. Volume 1. Field guide for pastoral grazing and
807 cropping on flat rolling country. 2nd Edition, Horizons Regional Council, Palmerston North, New
808 Zealand, pp. 119.

809

810 Shepherd, M., Newell-Price, P., 2013. Manure management practices applied to a seven-course
811 rotation on a sandy soil: effects on nitrate leaching. *Soil Use and Management* 29 (2), 210-219.

812

813 Singh, U., Sanabria, J., Austin, E.R., Agyin-Birikorang, S., 2011. Nitrogen Transformation,
814 Ammonia Volatilization Loss, and Nitrate Leaching in Organically Enhanced Nitrogen
815 Fertilizers Relative to Urea. *Soil Science Society of America* 76, 1842-1854.

816

817 Skiba, U., Jones, S.K., Dragosits, U., Drewer, J., Fowler, D., Rees, R.M., Pappa, V.A., Cardenas,
818 L., Chadwick, D., Yamulki, S., 2012. UK emissions of the greenhouse gas nitrous oxide.
819 *Philosophical Transactions of the Royal Society B: Biological Sciences* 367, 1175-1185.

820

821 Smith, K.A., Dobbie, K.E., Thorman, R., Watson, C., Chadwick, D., Yamulki, S. and Ball, B.,
822 2012. The effect of N fertiliser forms on nitrous oxide emissions from UK arable land and
823 grassland. *Nutrient Cycling in Agroecosystems* 93, 127-149.

824

825 Sommer, S.G., Olesen, J.E., 1991. Effects of dry matter content and temperature on ammonia
826 loss from surface-applied cattle slurry. *Journal of Environmental Quality* 20, 679-683.

827

828 Sommer, S., Hutchings, N., 2001. Ammonia emission from field applied manure and its
829 reduction-invited paper. *European Journal of Agronomy* 15, 1–15.

830

831 Sommer, S.G., Genermont, S., Cellier, P., Hutchings, N.J., Olesen, J.E., Morvan, T., 2003.
832 Processes controlling ammonia emission from livestock slurry in the field. *European Journal of*
833 *Agronomy* 19, 465-486.

834

835 Stocker, T.F, Qin, D., Plattner, G.K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y.,
836 Bex, V., Midgley, P.M., 2013. *The Physical Science Basis. Contribution of Working Group I to*
837 *the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge
838 University Press, Cambridge, pp 1-1535.

839

840 The Scottish Government. 2014. General Information. Guidance for farmers in nitrate vulnerable
841 zones. <http://www.gov.scot/Topics/farmingrural/Agriculture/Environment/NVZintro/NVZGuidanceforFarmers>,
842 accessed 17/06/2015.

843

844 Thorman, R.E., Hansen, M.N., Misselbrook, T.H., Sommer S.G., 2008. Algorithm for estimating
845 the crop height effect on ammonia emission from slurry applied to cereal fields and grassland.
846 *Agronomy for Sustainable Development* 28, 373-378.

847

848 Van der Hoek, K., 1998. Estimating ammonia emission factors in Europe: Summary of the work
849 of the UNECE ammonia expert panel. *Atmospheric Environment* 32 (3), 315-316.

850

851 Velthof, G., Kuikman, P., Oenema, O., 2003. Nitrous oxide emission from animal manures
852 applied to soil under controlled conditions. *Biology and Fertility of Soils* 37, 221-230.

853

854 Velthof, G.L., Mosquera, J., 2011. The impact of slurry application technique on nitrous oxide
855 emissions from agricultural soils. *Agriculture, Ecosystems and Environment* 140, 298-308.

856

857 Velthof, G.L., Hou, Y., Oenema, O. 2015. Nitrogen excretion factors of livestock in the European
858 Union: a review. *Journal of the Science of Food and Agriculture*, n/a.

859

860 Webb, J., Pain, B., Bittman, S., Morgan, J., 2010. The impacts of manure application methods on
861 emissions of ammonia, nitrous oxide and on crop response-a review. *Agriculture Ecosystems &*
862 *Environment* 137, 39-46.

863

864 Webb, J., Thorman, R., Fernanda-Aller, M., Jackson, D., 2014. Emission factors for ammonia
865 and nitrous oxide emissions following immediate manure incorporation on two contrasting soil
866 types. *Atmospheric Environment* 82, 280-287.

867

868 Wulf. S., Maeting, M., Bergmann, S., Clemens, J., 2001. Simultaneous measurement of NH₃,
869 N₂O and CH₄ to assess efficiency of trace gas emission abatement after slurry application.
870 *Phyton* 41 (3), 131-142.

871

872

Table 1. Manure properties and application rates for autumn and spring experiments. ND = not detectable; NM = not measured. The same cattle slurry was used in the ‘cattle slurry trailing hose’ and ‘cattle slurry surface broadcast’ treatments

Treatment	Time of application	Incorporated/ top-dressed	Fertiliser application rate (t ha ⁻¹)	Total N application rate (kg N ha ⁻¹)	Readily available N (kg N ha ⁻¹)			Total C application rate (kg C ha ⁻¹)	C:N ratio	Dry Matter (%)	pH
					NH ₄ ⁺ -N	NO ₃ ⁻ -N	Uric acid-N				
Broiler litter	Autumn	Incorporated	5.69	141	12.1	ND	NM	862	6.1	41.6	8.3
	Spring	Top-dressed	8.06	121	22.6	ND	1.9	729	6.0	26.6	8.9
Layer manure	Autumn	Incorporated	14.6	244	120.3	ND	NM	1001	4.1	21.8	8.0
	Spring	Top-dressed	16.4	228	91.3	ND	6.1	1111	4.9	21.8	8.6
Cattle slurry	Autumn	Incorporated	41.7	62.5	30.4	ND	NM	334	5.4	2.30	6.8
	Spring	Top-dressed	41.7	50	22.1	ND	NM	289	5.8	2.23	6.9
Cattle FYM	Autumn	Top-dressed	29.7	175	5.3	3.3	NM	2007	11.5	18.4	8.4

Table 2. The impact of manure type on annual cumulative N₂O emissions, N₂O EFs, cumulative NH₃ emissions, NH₃ EFs, total N loss as % N applied, and annual direct + indirect N₂O emissions when applied in autumn and spring respectively: Transformed (Tr) and back transformed (Back Tr) values. When a significant effect between fertilisers is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Season-Treatment	Cumulative N ₂ O emissions (kg N ₂ O-N ha ⁻¹)		N ₂ O EF (%)		Cumulative NH ₃ emissions (kg NH ₃ -N ha ⁻¹)#	NH ₃ EF (%)		Total N loss as % N applied		Annual direct + indirect N ₂ O (kg N ₂ O-N ha ⁻¹)	
	Tr ¹	Back Tr	Tr ²	Back Tr		Tr ³	Back Tr	Tr ⁴	Back Tr	Tr ⁵	Back Tr
	A-Con	-0.40	0.63	-		-	-	-	-	-	-
A-BL	1.05	2.20	0.06 ^{bc}	1.07	3.60 ^{ab}	1.13 ^b	2.54	2.05 ^b	4.10	1.32 ^{bc}	2.55
A-LM	1.27	2.48	-0.56 ^{ab}	0.56	39.23 ^c	5.08 ^d	16.02	6.28 ^d	17.14	1.97 ^c	3.45
A-CSSB	1.10	2.26	0.80 ^c	2.17	5.54 ^b	3.25 ^c	8.14	4.96 ^c	12.11	1.26 ^{bc}	2.47
A-CSTH	1.09	2.25	0.70 ^c	1.96	5.33 ^b	3.28 ^c	8.02	4.91 ^c	11.94	1.24 ^{bc}	2.44
A-CFYM	0.27	1.28	-1.22 ^a	0.27	0.69 ^a	-0.97 ^a	0.29	0.09 ^a	1.09	0.62 ^{ab}	1.67
LSD	NS		1.00		4.00	1.55		1.27		1.18	

	Tr ⁶	Back Tr	Tr ⁷	Back Tr	Tr ⁸	Back Tr	Tr ⁹	Back Tr	Tr ¹⁰	Back Tr	Tr ¹¹	Back Tr
S-Con	0.66 ^b	0.95	-	-	-	-	-	-	-	-	0.58 ^b	0.90
S-BL	0.54 ^b	0.74	2.19	0.34	3.88 ^b	17.67	6.69	14.69	8.23	15.34	0.71 ^{bc}	1.20
S-LM	0.57 ^b	0.79	2.08	0.20	5.26 ^c	36.38	7.15	16.06	8.71	16.44	0.88 ^c	1.68
S-CSSB	-0.14 ^a	-0.08	1.08	-1.02	2.76 ^{ab}	9.00	7.95	18.56	9.64	18.63	0.08 ^a	0.13
S-CSTH	-0.15 ^a	-0.09	1.04	-1.07	1.95 ^a	5.19	5.45	11.24	6.36	11.28	0.03 ^a	0.08
LSD	0.26		NS		1.30		NS		NS		0.21	

Transformations of non-normal data for statistical analysis: ¹((kgN₂O**0.7)-1)/0.7 ²((N₂O EF**0.1)-1)/0.1 ³((NH₃ EF**0.4)-1)/0.4 ⁴((Total N loss as %N applied**0.5)-1)/0.5 ⁵((Direct + indirect N₂O**0.7)-1)/0.7 ⁶((kgN₂O + 0.95)**0.1)-1)/0.1 ⁷((N₂O EF + 3.2)**0.8)-1)/0.8 ⁸((kgNH₃**0.2)-1)/0.2 ⁹((NH₃ EF**0.6)-1)/0.6 ¹⁰((Total N loss as %N applied**0.7)-1)/0.7 ¹¹((Direct + indirect N₂O + 0.95**0.2)-1)/-0.2
no transformation required

Table 3. The impact of season of application, manure type and their interactions on annual cumulative N₂O emissions, N₂O EFs, cumulative NH₃ emissions, NH₃ EFs, total N loss as % N applied, and annual direct + indirect N₂O emissions. Transformed (Tr) and back transformed (Back Tr) values. When a significant effect is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

	Cumulative N ₂ O emissions (kg N ₂ O-N ha ⁻¹) #	N ₂ O EF (%)		Cumulative NH ₃ emissions (kg NH ₃ -N ha ⁻¹) #	NH ₃ EF (%)		Total N loss as % N applied#	Annual direct + indirect N ₂ O (kg N ₂ O-N ha ⁻¹) #
		Tr ¹	Back Tr		Tr ²	Back Tr		
Autumn	2.00 ^a	3.55	1.72	13.42	4.23	8.21	11.44	2.34 ^a
Spring	0.35 ^b	1.76	-0.33	17.58	6.81	15.04	15.71	0.69 ^b
Con	0.51	-	-	-	-	-	-	0.51 ^a
BL	1.48	2.68	0.71	10.73 ^a	3.97 ^a	7.62	9.75	1.89 ^{bc}
LM	1.68	2.48	0.48	38.05 ^b	7.15 ^b	16.06	16.82	2.59 ^c
CSSB	1.12	2.76	0.80	7.56 ^a	6.12a ^b	13.06	15.75	1.33 ^{ab}
CSTH	1.10	2.71	0.74	5.67 ^a	4.83 ^a	9.65	11.97	1.28 ^{ab}
A-Con	0.68	-	-	-	-	-	-	0.68
S-Con	0.33	-	-	-	-	-	-	0.33
A-BL	2.20	3.00	1.08	3.60 ^a	1.25	2.54	4.11	2.55
S-BL	0.77	2.37	0.36	17.85 ^b	6.69	14.69	15.39	1.22
A-LM	2.55	2.73	0.77	39.23 ^c	7.14	16.03	17.12	3.50
S-LM	0.80	2.23	0.20	36.86 ^c	7.15	16.06	16.52	1.68
A-CSSB	2.31	4.27	2.57	5.54 ^a	4.30	8.38	12.46	2.51
S-CSSB	-0.06	1.24	-0.90	9.59 ^a	7.95	18.56	19.05	0.15
A-CSTH	2.27	4.22	2.51	5.33 ^a	4.22	8.19	12.07	2.47
S-CSTH	-0.08	1.20	-0.94	6.01 ^a	5.45	11.24	11.87	0.09
Season LSD	0.75	NS		NS	NS		NS	0.75
Treatment LSD	NS	NS		5.17	2.18		NS	0.93
Season*treatment LSD	NS	NS		7.46	NS		NS	NS

Transformations of non-normal data for statistical analysis ¹((kg N₂O+0.95)**0.6)-1/0.6 ²((NH₃ EF**0.6)-1)/0.6 # no transformation required

Table 4. The impact of manure type on grain yield, N₂O and NH₃ yield intensity, and grain N uptake when applied in autumn and spring, respectively: Transformed (Tr) and back transformed (Back Tr) values. When a significant effect between fertilisers is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

Season-Treatment	Grain yield @ 85% DM (t ha ⁻¹)#		N ₂ O + NH ₃ yield intensity (kg N ₂ O-N and NH ₃ -N t ⁻¹ grain DM)#	Grain N uptake (kg N ha ⁻¹)#
	Tr ¹	Back Tr		
A-Con	2.38 ^a		0.29 ^a	31.86 ^a
A-BL	3.48 ^c		1.67 ^b	48.72 ^{bc}
A-LM	2.90 ^{abc}		14.45 ^e	38.83 ^{ab}
A-CSSB	2.45 ^a		3.32 ^d	33.37 ^a
A-CSTH	2.77 ^{ab}		2.74 ^c	39.31 ^{abc}
A-CFYM	3.37 ^{bc}		0.59 ^a	49.70 ^c
LSD	0.69		1.09	10.48
	Tr ¹	Back Tr		
S-Con	0.60 ^a	1.71	0.33 ^a	22.70 ^a
S-BL	1.35 ^b	2.94	6.43 ^c	41.60 ^{ab}
S-LM	2.28 ^c	5.05	7.42 ^c	70.60 ^c
S-CSSB	1.61 ^{bc}	3.47	2.83 ^b	48.00 ^b
S-CSTH	1.33 ^b	2.91	2.08 ^b	40.30 ^{ab}
LSD	0.72		1.04	22.34

Transformations of non-normal data for statistical analysis: ¹((grain yield**0.4)-1)/0.4 # no transformation required

Table 5. The impact of season of application, manure type and their interactions on grain yield, N₂O and NH₃ yield intensity, and grain N uptake: Transformed (Tr) and back transformed (Back Tr) values. When a significant effect is present, transformed values that do not share a letter are significantly different. A = autumn; S = spring; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose. Fertiliser application rates are displayed in Table 1. Details of the transformation applied to normalise the data for statistical analysis are displayed below. NS = not significant. LSD = least significant difference.

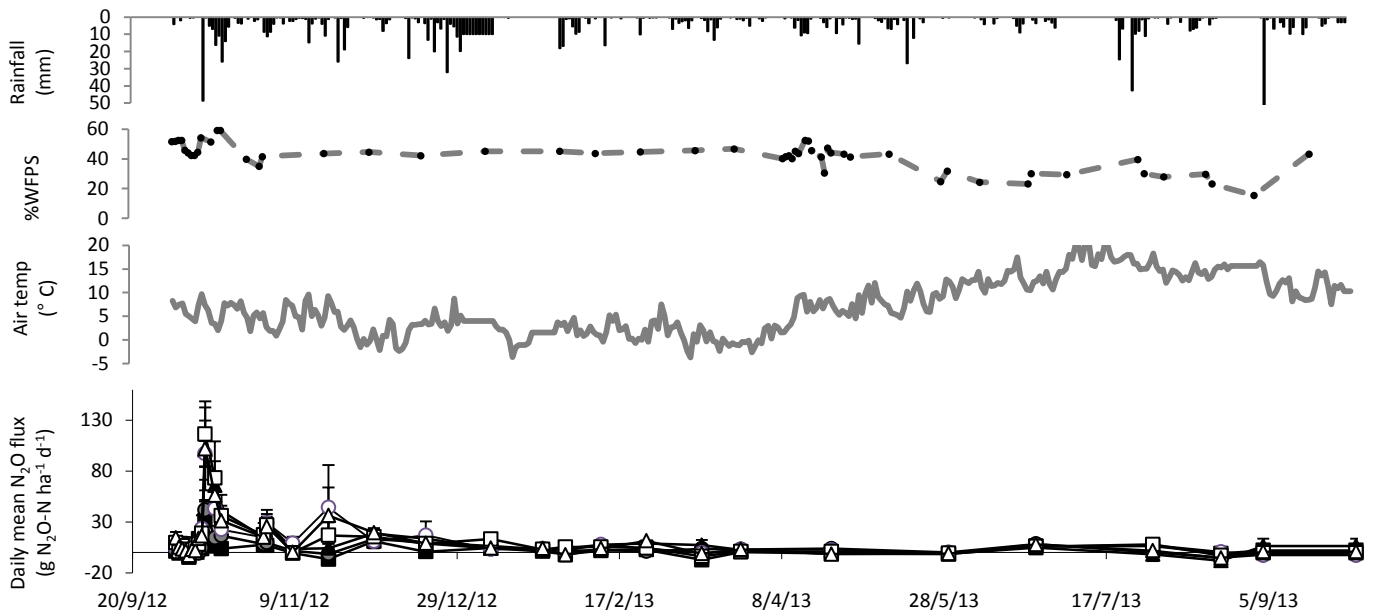
	Grain yield @ 85% DM (t ha ⁻¹)		N ₂ O + NH ₃ yield intensity (kg N ₂ O-N and NH ₃ -N t ⁻¹ grain DM) #	Grain N uptake (kg N ha ⁻¹)	
	Tr ¹	Back Tr		Tr ²	Back Tr
Autumn	1.12	2.75	4.49	5.34	37.82
Spring	1.25	3.05	3.82	5.53	41.35
Con	0.75 ^a	2.01	0.31 ^a	4.62 ^a	26.36
BL	1.31 ^{bc}	3.20	4.05 ^c	5.70 ^{bc}	44.88
LM	1.55 ^c	3.86	10.93 ^d	6.04 ^c	52.48
CSSB	1.17 ^b	2.86	3.07 ^b	5.37 ^b	38.37
CSTH	1.15 ^b	2.82	2.41 ^b	5.43 ^b	39.50
A-Con	0.93 ^{ab}	2.35	0.29 ^a	4.96 ^{ab}	31.37
S-Con	0.56 ^a	1.70	0.33 ^a	4.28 ^a	22.02
A-BL	1.42 ^c	3.49	1.67 ^{ab}	5.88 ^{cd}	48.79
S-BL	1.20 ^{bc}	2.93	6.43 ^c	5.52 ^{bc}	41.23
A-LM	1.19 ^{bc}	2.91	14.45 ^d	5.39 ^{bc}	38.75
S-LM	1.91 ^d	5.04	7.42 ^c	6.70 ^d	70.16
A-CSSB	0.96 ^{abc}	2.41	3.32 ^b	5.07 ^{abc}	33.14
S-CSSB	1.38 ^{bc}	3.38	2.83 ^b	5.67 ^{bc}	44.26
A-CSTH	1.12 ^{bc}	2.75	2.74 ^b	5.39 ^{bc}	38.75
S-CSTH	1.19 ^{bc}	2.91	2.08 ^{ab}	5.46 ^{bc}	40.07
Season LSD	NS		NS	NS	
Treatment LSD	0.32		0.81	0.57	
Season*treatment LSD	0.49		1.87	0.89	

Transformations of non-normal data for statistical analysis: ¹((grain yield**0.2)-1)/0.2 ²((grain N uptake**0.2)-1)/0.2 # no transformation required

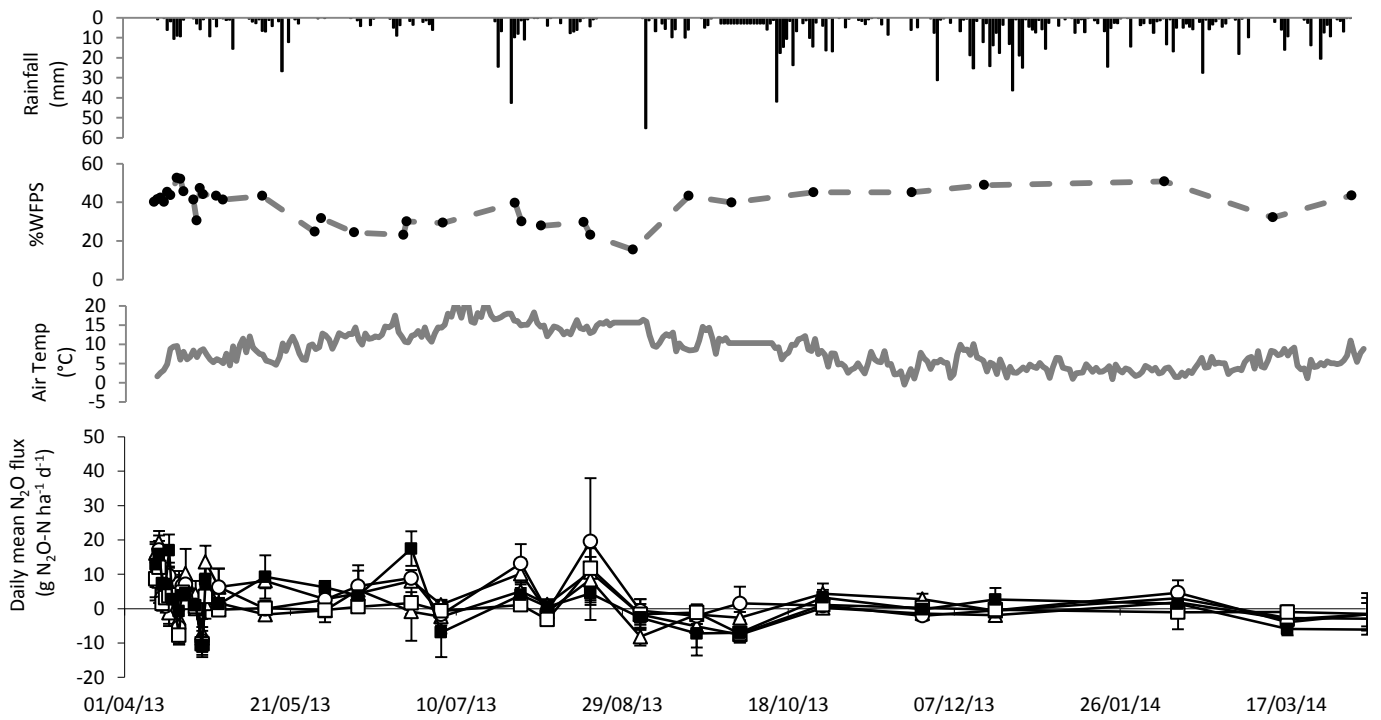
Supplementary Table 1. The mean and standard error (SE) (n = 3) of annual cumulative N₂O emissions, N₂O emission factors (EFs), cumulative NH₃ emissions, NH₃ EFs, total N loss as % N applied, annual direct + indirect N₂O, grain yield, N₂O + NH₃ yield intensity, and grain N uptake before data transformation for statistical analysis. Treatment rates and manure composition data are displayed in Table 1. A = autumn application; S = spring application; Con = control; BL = broiler litter; LM = layer manure; CSSB = cattle slurry surface broadcast; CSTH = cattle slurry trailing hose; CFYM = cattle farmyard manure

		Cumulative N ₂ O (kg N ₂ O-N ha ⁻¹)		N ₂ O EF (%)		Cumulative NH ₃ (kg NH ₃ -N ha ⁻¹)		NH ₃ EF (%)		Total N loss as % N applied		Annual direct + indirect N ₂ O (kg N ₂ O-N ha ⁻¹)		Grain yield @ 85% DM (t ha ⁻¹)		N ₂ O + NH ₃ yield intensity (kg N ₂ O-N and NH ₃ -N t ⁻¹ grain DM)		Grain N uptake (kg N ha ⁻¹)	
		Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
A	Con	0.68	0.29	-	-	-	-	-	-	-	-	0.68	0.29	2.38	0.31	0.29	0.13	31.86	4.56
	BL	2.20	0.12	1.08	0.12	3.60	0.35	2.55	0.24	4.11	0.29	2.55	0.13	3.48	0.05	1.67	0.14	48.72	0.62
	LM	2.55	0.83	0.77	0.46	39.23	1.48	16.03	0.60	17.12	0.41	3.50	0.82	2.90	0.16	14.45	0.50	38.83	2.73
	CSSB	2.31	0.61	2.59	0.96	5.54	2.17	8.86	3.47	12.46	2.93	2.51	0.60	2.45	0.34	3.32	0.77	33.37	3.32
	CSTH	2.27	0.47	2.53	1.15	5.33	1.58	8.53	2.52	12.07	1.78	2.47	0.45	2.77	0.26	2.74	0.29	39.31	5.36
	CFYM	1.28	0.04	0.34	0.16	0.69	0.44	0.39	0.25	1.12	0.27	1.68	0.05	3.37	0.10	0.59	0.16	49.70	3.71
S	Con	0.33	0.70	-	-	-	-	-	-	-	-	0.33	0.70	1.75	0.31	0.33	0.53	22.70	4.10
	BL	0.77	0.21	0.36	0.49	17.85	1.96	14.75	1.62	15.39	1.53	1.22	0.20	2.94	0.23	6.43	0.85	41.61	4.84
	LM	0.80	0.11	0.21	0.30	36.86	4.60	16.17	2.02	16.52	2.06	1.68	0.16	5.06	0.32	7.42	0.66	70.59	6.84
	CSSB	-0.06	0.13	-0.79	1.51	9.59	2.83	19.18	5.66	19.05	5.41	0.15	0.10	3.64	0.99	2.83	0.65	48.00	13.77
	CSTH	-0.08	0.10	-0.83	1.49	6.01	2.37	12.03	4.75	11.87	4.71	0.09	0.10	2.90	0.06	2.08	0.86	40.34	3.13

Figure 1.



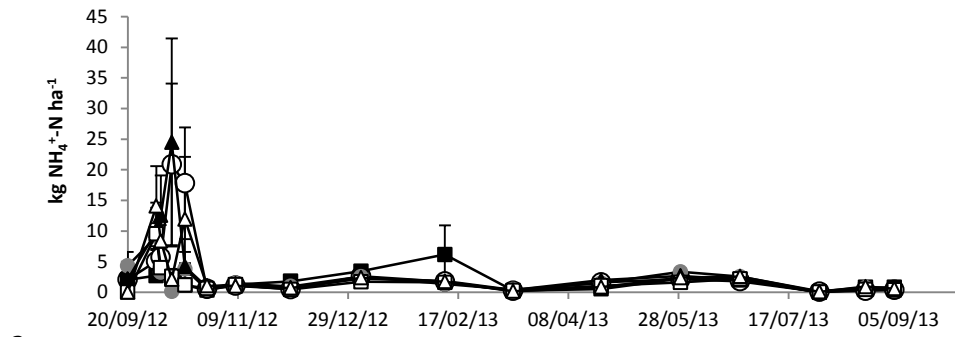
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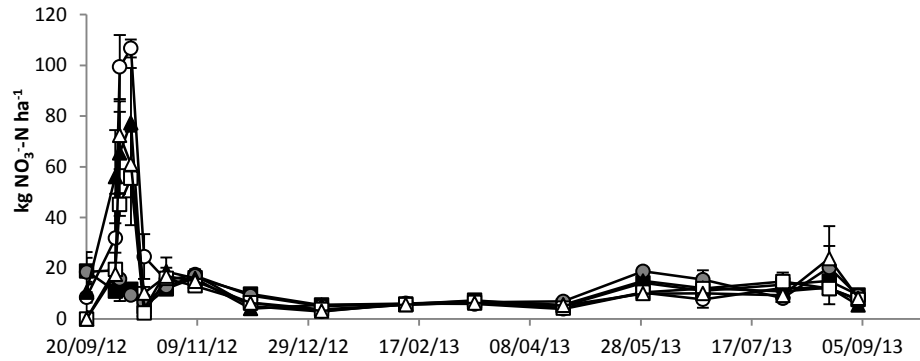
b.

Con
 CFYM
 BL
 LM
 CSSB
 CSH

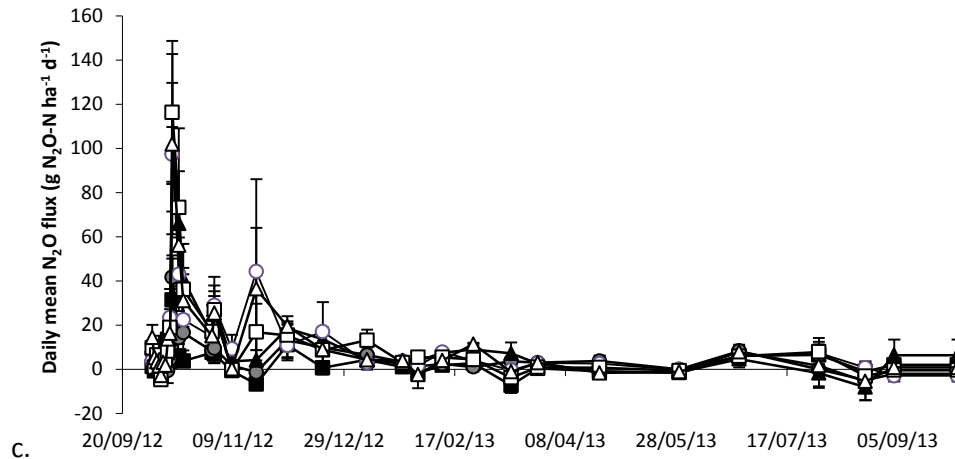
Figure 2.



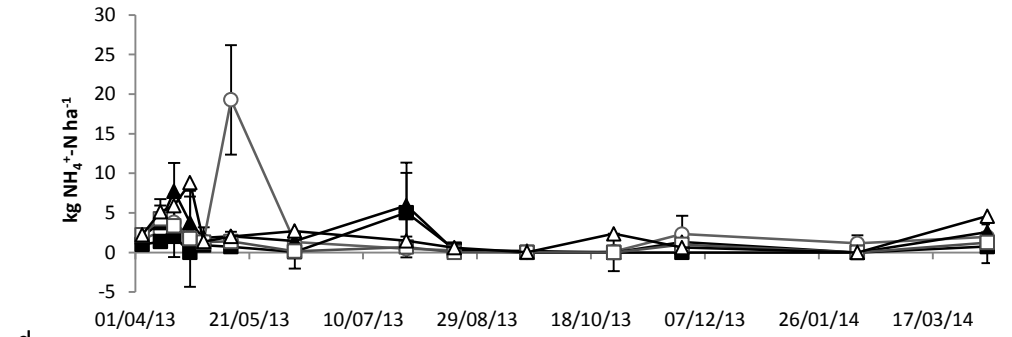
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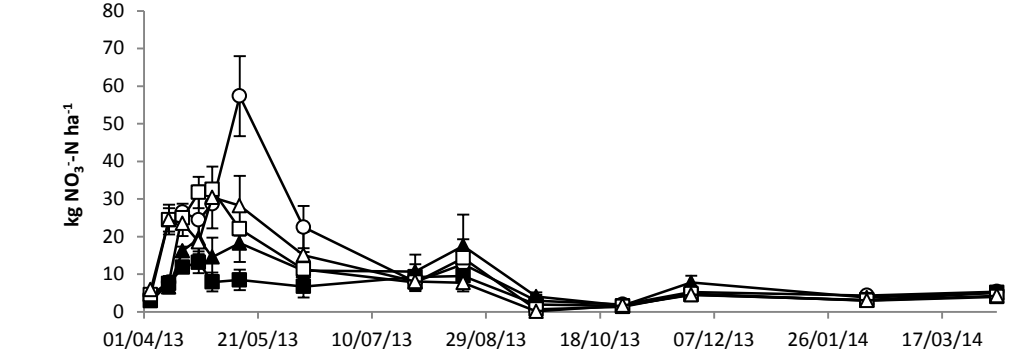
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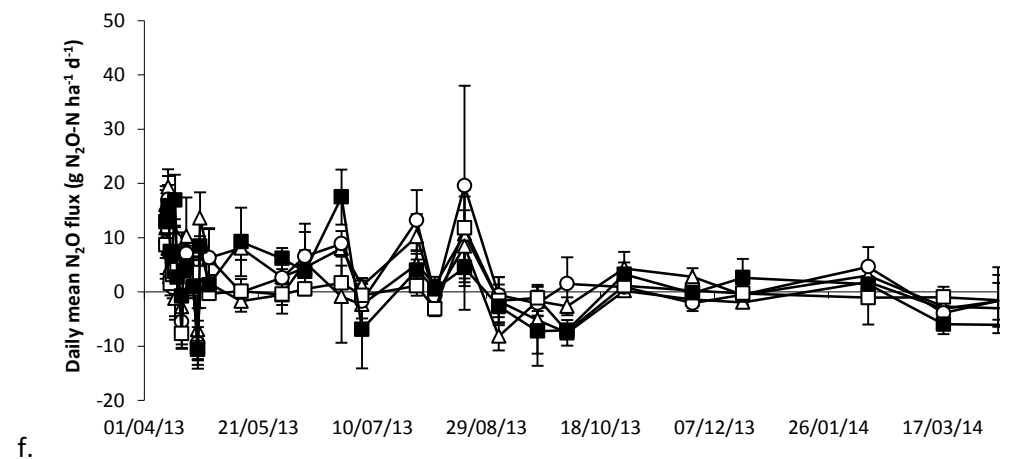
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d.



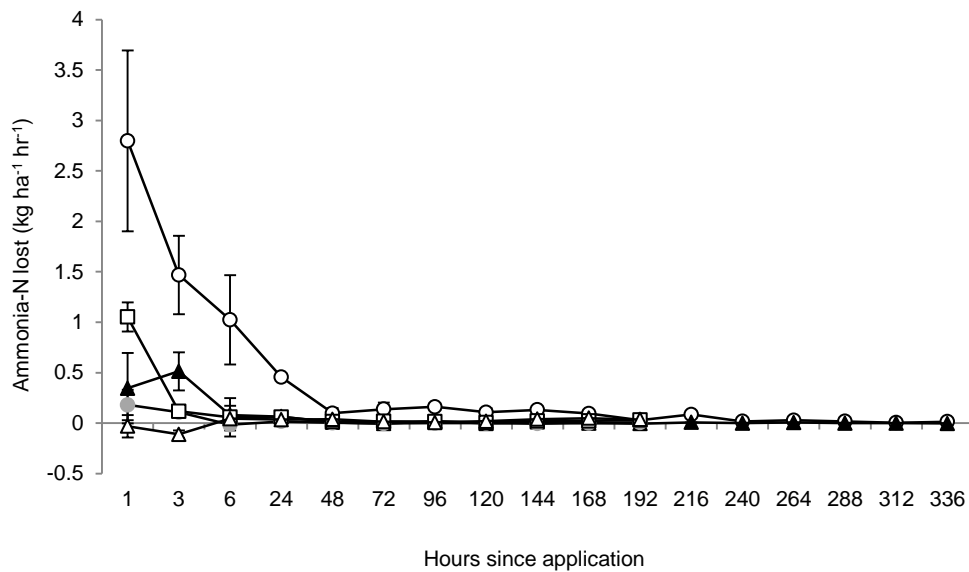
e.



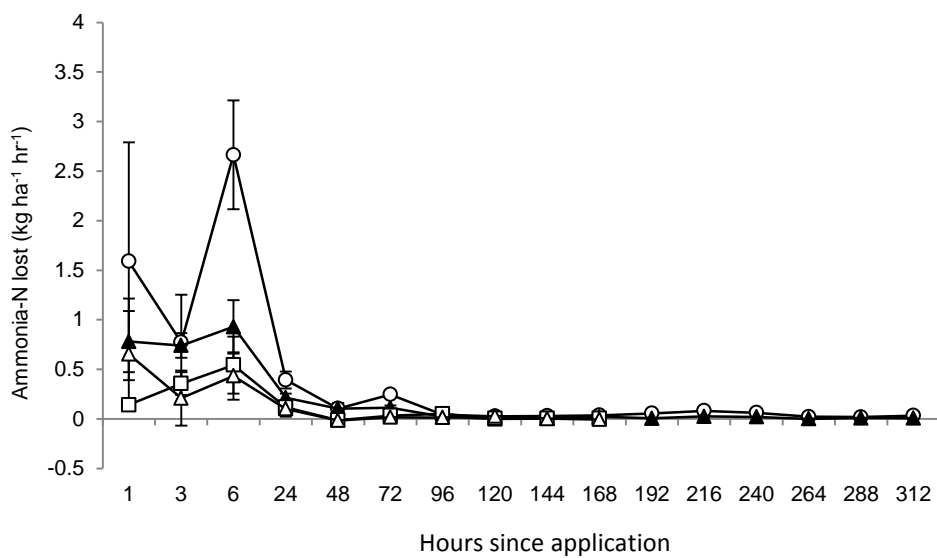
f.

Con
 CFYM
 BL
 LM
 CSSB
 CSTH

Figure 3.



a.



b.

—●— CFYM —▲— BL —○— LM —□— CSSB —△— CSTH

Figure captions

Fig.1. Variation in daily rainfall, soil water filled pore space (%WFPS) and air temperature throughout the experimental periods, and their relationship with daily N₂O emissions. **a.** autumn experimental year; **b.** spring experimental year. Error bars on the N₂O data indicate the SE of the mean, n = 3. LM = layer manure; CFYM = cattle farmyard manure; CSSB = cattle slurry surface broadcast; Con = control; BL = broiler litter; CSTH = cattle slurry trailing hose

Fig.2.a. Variation in soil NH₄⁺-N following manure application in autumn. **b.** Variation in soil NO₃⁻-N following manure application in autumn **c.** daily N₂O emissions following manure application in autumn. **d.** Variation in soil NH₄⁺-N following manure application in spring **e.** Variation in soil NO₃⁻-N following manure application in spring **f.** daily N₂O emissions following manure application in spring. Error bars indicate the standard error of the mean (n = 3). LM = layer manure; CFYM = cattle farmyard manure; CSSB = cattle slurry surface broadcast; Con = control; BL = broiler litter; CSTH = cattle slurry trailing hose. Note – use of different scales on the Y axis in the autumn (a, b, c) and spring (d, e, f) graphs to provide clarity of soil mineral N and N₂O flux data

Fig.3. The variation in NH₃ emissions following manure applications (LM = layer manure; CFYM = cattle farmyard manure; CSSB = cattle slurry surface broadcast; Con = control; BL = broiler litter; CSTH = cattle slurry trailing hose) to arable land in autumn and spring. **a.** autumn experiment; **b.** spring experiment. Error bars on the NH₃ data indicate the SE of the mean, n = 3.