Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley

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1 **Title: Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide**

2 **emissions in spring barley**

3

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12

13 **Abstract**

14 The application of nitrogen (N) fertilisers to agricultural soils is a major source of nitrous

15 oxide (N_2O) emissions. The Intergovernmental Panel on Climate Change (IPCC) has set a

16 default emission factor of 1% (EF_1) for N fertiliser applied to managed agricultural soils. This

17 value does not differentiate between different N fertiliser formulations or rates of N

18 application. The objective of this field study under spring barley was to determine N_2O EF's

19 for different N fertiliser formulations including urea and urea stabilised with the nitrification

20 inhibitor dicyandiamide (DCD) and/or the urease inhibitor *N*-(*n*-butyl) thiophosphoric

21 triamide (NBPT) and to evaluate their N_2O loss abatement potential relative to calcium

22 ammonium nitrate (CAN). The highest EF_1 measured was 0.49% for CAN which was less

23 than half the IPCC default value of 1%. While the urease inhibitor did not reduce emissions

24 relative to CAN; the nitrification inhibitor significantly reduced emissions compared to CAN

25 with EF_1 as low as 0.00% for a typical spring barley site. There was no significant impact of

26 CAN or urea application rate on EF_1 but there was a significant negative relationship

27 observed for urea in 2013. The study highlights the importance of generating higher Tier

28 emission factors in terms of fertiliser type for use in national inventories.

29

30 **Keywords:** urea; emission factor; arable soil; DCD; Inhibitors; NBPT

31

1 Introduction

Concentrations of atmospheric greenhouse gases (GHGs) have increased since the beginning of the industrial era, due to anthropogenic activities (U.S. EPA, 2015). Between 1990 and 2005, global non-carbon dioxide (CO_2) GHG emissions grew by 10% to approximately 10,800 megatons CO_2 equivalent (Mt CO_2 eq) and are expected to increase by 43% by 2030 (U.S. EPA, 2012). Globally, the agriculture sector accounts for the largest proportion of non-CO_2 GHG emissions, accounting for 54% in 2005 (U.S. EPA, 2012). Nitrous oxide comprises approximately 32% of agricultural emissions (U.S. EPA, 2012) and is a potent GHG, with a global warming potential 265 times that of CO_2 over a 100 year time frame (Myhre et al., 2013). The atmospheric concentration of N_2O has increased at an average rate of 0.75 ppb yr^{-1}, rising 20% since 1750 to 324 ppb (IPCC, 2014). Emissions associated with nitrogen (N) application to agricultural soils comprise 60% of global N_2O emissions and are projected to increase from 6.1 to over 7 Tg N_2O-N yr^{-1} by 2030, due to increased global population and food demand (Reay et al., 2012). The use of mineral fertilisers has been one of the principal drivers of this increase in emissions (Davidson, 2009). Excess N application has resulted in enhanced reactive N losses to the environment (Bell et al., 2015). Furthermore N_2O is the single most important ozone-depleting gas and is expected to remain so throughout the 21st century (Ravishankara et al., 2009).

In order to generate total N_2O emissions for inputting into national inventories, the quantity of a given activity (e.g. tonnes of fertiliser applied) is multiplied by an emission factor (EF). This emission factor is defined as the percentage of N_2O emitted as a proportion of the N applied. The IPCC default EF for direct N_2O emissions, associated with the application of mineral or organic fertiliser to managed soils, (termed EF_1) is 1% of the N applied (IPCC, 2006). This value is a crude estimate as it does not account for crop and soil type, climatic conditions or management practices, all of which affect N_2O emissions (Dobbie and Smith,

57 2003a, 2003b; Dobbie et al., 1999; Lesschen et al., 2011). Country and cropping system

58 specific data would allow temperate regions to use the Tier 2 emission inventory

59 methodology, where these more detailed and accurate emission factors that are specific for

60 soil and crop type are required (IPCC, 2006). Subsequently, these data could support the

61 development of new N fertiliser recommendations in Ireland; therefore promoting continued

62 reductions of GHG emissions in line with the 2030 targets to reduce GHG emissions by 40%

63 (EC, 2014).

64 In Ireland the agricultural sector contributes 32% of national GHG emissions (Duffy et al.,

65 2015). Nitrogen application to agricultural soils is one of the key categories, accounting for

66 22% of total emissions from agriculture and this is projected to increase by 12% by 2020

67 (EPA, 2013). The focus of this study is on arable land, specifically examining the N_2O

68 emissions resulting from the addition of N fertiliser to spring cereal crops, which is one of the

69 largest contributors to GHGs from this land use type. Altering fertiliser formulation and/or

70 rate as well as the incorporation of inhibitors may be a key abatement strategy for reducing

71 N_2O emissions from agriculture (Harty et al., 2016).

72 Calcium ammonium nitrate (CAN) is the dominant N fertiliser used by arable farmers in

73 Ireland. CAN contains 27% N, of which 50% is in the nitrate-N form and immediately

74 contributes to the soil nitrate pool. Nitrate is then available for N_2O loss through the

75 denitrification processes. Nitrification may also be an important source of N_2O from the

76 application of urea or ammonium based fertilisers (Bremner and Blackmer, 1978).

77 Substituting CAN with urea as an alternative N fertiliser formulation has the potential to

78 reduce direct N_2O emissions, associated with denitrification, because urea or ammonium N

79 forms are not immediately available for denitrification after application. However, there is

80 potential for nitrifier denitrification to be a source of N_2O (Kool et al., 2011) coupled with the

81 potential for urea to favour N loss as ammonia during urea hydrolysis. The addition of a

82 urease inhibitor has potential to reduce ammonia volatilisation which not only contributes to

83 air pollution but which can also contribute to indirect N_2O emissions (Watson et al., 2009;

84 Forrestal et al., 2015). The addition of a nitrification inhibitor has potential to regulate the soil

85 nitrate pool and further reduce direct N_2O emissions by both nitrification and denitrification

86 (Dobbie and Smith, 2003a). The rate of N fertiliser application is also important as generally

87 the higher the N fertiliser rate, the higher the N_2O emissions (Hinton et al., 2015). Using the

88 IPCC default EF_1 assumes a linear relationship between N_2O emissions and N fertiliser rate

89 which Hinton et al (2015) observed. Other studies have observed nonlinear relationships

90 between N_2O emissions and N fertiliser rate (Hoben et al., 2011; McSwiney and Roberston,

91 2005).

92 In this study, N_2O emissions were measured from spring barley after fertiliser applications of

93 CAN and urea with and without N stabilisers. Nitrogen stabilisers are fertiliser additives that

94 reduce environmental N losses thereby stabilising the N in the soil. These can either a) reduce

95 urea N loss via volatilisation and are termed urease inhibitors or reduce N loss via

96 denitrification of nitrate and are termed nitrification inhibitors. These stabilisers can thus

97 increase fertiliser use efficiencies by increasing plant N uptake and crop yields. The N

98 stabilisers evaluated in this study were the urease inhibitor N-(n-butyl) thiophosphoric

99 triamide (NBPT (trade name Agrotain™) and also referred to as n-BTPT in other studies), the

100 nitrification inhibitor dicyandiamide (DCD), and the Maleic-Itaconic acid Co-polymer

101 (MICO (trade name NutriSphere-N®)) which is a urease and nitrification inhibitor. The aims

102 of this study were to quantify the effect of N fertiliser rate and formulation on direct N_2O

103 emissions from spring barley in a temperate maritime climate and to develop crop specific

104 emission factors for use in national N_2O emissions inventories. The hypothesis of this study

105 is that changing N fertiliser source from CAN to stabilised urea reduces N_2O emissions.

106

2 Materials and Methods

2.1 Site description

Field plot trials were conducted on spring malting barley on a free-draining loam soil located in Marshalstown, Co. Wexford (Table 1). This field site was located within the main malting barley growing region in Ireland (Duffy et al., 2015) and was representative of the typical soil type used for arable cropping. The site history was long term arable production for at least 20 years.

2.2 Crop husbandry

The spring barley (*Hordeum vulgare* L.) cultivar used was 'Sebastian'. The site was ploughed to approximately 20 cm depth in February 2013 and March 2014. The crop was sown in mid-April in both years and was harvested in mid-August in both years. The experiment ran from April 2013 to April 2015 and generated emission factors for two years (crop sowing time to the following sowing time each year). The site characteristics are described in Table 1 and are based on the top 10 cm of soil which is the standard agronomic soil sampling depth in Ireland. Each year basal P, K and S were applied to the soil, according to the Teagasc Green Book of nutrient advice (Coulter and Lalor, 2008) to prevent nutrient deficiencies from occurring. A robust pesticide programme was applied to the crop to control weeds, pests and diseases as per standard agronomic practice for spring barley crops (Teagasc, 2015).

132   *Table 1*. Site location and soil characteristics (0-10 cm depth)

GPS Co-ordinates	52° 33' 37.3" N 6° 36' 09.0" W
Drainage Class	Free- draining
Texture	Loam
Sand %	31.8
Silt %	41.4
Clay %	26.8
Stone volume (v/v)	28
pH	6.76
LOI %	8.99
Total C %	2.88
Total N %	0.281
C : N ratio	10
CEC (meq/100g)	21.1
Ca (mg/kg soil)	1616
K (mg/kg soil)	267
Mg (mg/kg soil)	164
P (mg/kg soil)	37.3
S (mg/kg soil)	4.8

133

134

135   2.3 Experimental Design

136   A randomised block design was used with five replicates of each fertiliser formulation. In

137   addition to the unfertilised control, six fertiliser formulations were used: (i) CAN, (ii) urea

138   (iii) urea + NBPT (iv) urea + DCD (v) urea + NBPT + DCD, and (vi) urea + MICO included

139   in 2014 only. All fertiliser formulations were applied at the common N rate of 150 kg N ha^{-1}

140 as this was the recommended N rate for spring barley as per the target crop yield. CAN and

141 urea were applied at additional rates and details of the N fertiliser rates used are shown in

142 Table 2. Each experimental unit (trial plot) measured 6m by 2.5m. Fertiliser was applied in

143 two splits for all treatments. The first split comprised 30 kg N ha^{-1} and was surface applied

144 within seven days of sowing. The second split was comprised of the remaining N fertiliser to

145 make up the individual treatment rate (for 150 kg N ha^{-1} the 2nd split was 120 kg N h^{-1}) and

146 was applied during early to mid-tillering (Zadoks GS 20-25). The first split fertiliser was

147 applied 15th April 2013 and the 23rd April 2014. The second split was applied 13th May in

148 both years. Pre-weighed fertiliser was applied by hand to the chamber base separately to the

149 plot area to ensure the correct N application rate within the chambers.

150

151 *Table 2.* Nitrogen fertiliser formulations and rate

Fertiliser Formulation	N Rate (kg N ha^{-1})				
	100	125	150	175	200
CAN	✓	✓	✓	✓	✓
Urea	✓	✓	✓		✓
Urea + NBPT			✓		
Urea + DCD			✓		
Urea + NBPT + DCD			✓		
Urea + MICO			✓		

152

153

154 *2.4 Soil and Climatic Analysis*

155 Total daily rainfall, air temperature and humidity were recorded at a weather station adjacent

156 to the site. Atmospheric pressure from the nearest available weather station at Johnstown

157 Castle was used. Soil moisture was recorded on each day of N_2O measurement to a depth of

158   10 cm using a Delta T ML2 probe (Delta-T Devices, Burwell, Cambridge, UK). In addition

159   to this, soil samples were taken on a weekly basis at the beginning of the year and on each

160   day of measurement once the frequency of N_2O measurement was reduced later in the

161   growing season. The gravimetric water content (GWC) of the soil was measured using these

162   soil samples. Soil samples were taken to 10 cm depth using a soil corer (2 cm diameter). Five

163   cores were taken from each plot, bulked together in sealed plastic bags and placed in a cool-

164   box. Following sampling (i.e. within 2 hours) the soil samples were taken to the laboratory

165   where they were wet sieved to 2 mm followed immediately by mineral N extraction using 2*M*

166   potassium chloride (KCl) (1:5 ratio of soil to KCl) (Keeney and Nelson, 1982; Mulvaney,

167   1996). The mineral N extracts were analysed colorimetrically using an Aquakem 600A

168   (Aquakem 600A, 01621, Vantaa, Finland) to determine the concentration of the mineral N

169   species i.e. Total Oxidised N (TON (including nitrite (NO_2^-) and nitrate (NO_3^-)) and

170   ammonium-N (NH_4^+-N). Soil sampling and mineral N extraction occurred weekly at the

171   beginning of the experiment and was reduced to once fortnightly coinciding with the

172   frequency of N_2O measurements. The gravimetric water content (GWC) of the soil samples

173   was also measured on each day of sampling .Soil bulk density was measured four times over

174   the course of the experiment (after the crop was planted and after harvest) and this was used

175   with GWC to calculate volumetric water content (VWC). Soil bulk density and VWC were

176   used to calculate water filled pore space percentage (WFPS %)

177

178   *2.5 Nitrous oxide (N_2O) sampling and analysis*

179   Daily N_2O fluxes were measured using the static chamber technique (Smith et al., 1995;

180   Chadwick et al., 2014), adhering to the methodology guidelines compiled by the Global

181   Research Alliance (de Klein and Harvey, 2012). The N_2O chamber measurement area was

182     $0.4m^2$. Collars were installed to at least 5 cm into the soil (Smith et al., 2012) and contained a

183   neoprene filled channel in order to maintain an air-tight seal. Collars were installed at least

184   three days prior to the first sampling and were left in place for the duration of the study.

185   Collars were removed for harvest and ploughing events and then reinstalled afterwards.

186   When sampling, a stainless steel lid was placed onto the collar and a 10 kg weight was placed

187   on top to compress the neoprene gasket, thus ensuring an airtight seal inside the chamber.

188   There were two different chamber sizes. A chamber with air volume 0.017 m^3 (10cm height)

189   was used from sowing until Zadoks GS 32-33 (stem extension). Subsequently, larger

190   chambers with an air volume of 0.096m^3 (60cm height) were used until harvest, after which

191   small chambers were used again. Chambers were sampled prior to fertilisation, and then on a

192   reducing temporal resolution for four weeks after fertiliser was applied i.e. four times per

193   week for the first two weeks, twice per week for the next two weeks, and once per week

194   thereafter. This sampling frequency was adopted to capture the period of most active N loss

195   in more detail. In Year two, N_2O sampling was reduced to once every three weeks (after the

196   initial four weeks of sampling after fertilisation) after reviewing year one data. The chamber

197   lids were left on for 40 minutes, (larger chamber lids were left on for 60 minutes), then a 10

198   ml sample was taken from each chamber and immediately injected into a 7 ml pre-evacuated

199   exetainer (Sigma-Aldrich, UK) fitted with double wadded septa (Labco, High Wycombe,

200   UK). On each sampling date eight samples of ambient air were taken around the site and the

201   average used as time zero (T0) sample for each chamber. Chadwick et al. (2014) have shown

202   that ambient samples are a useful surrogate for individual chamber T0 samples. On each

203   sampling day, five chambers were chosen at random to check for linearity. These chambers

204   were sampled at T0, T15, T30, T40, T60 and samples were statistically analysed to test for

205   flux/no flux, quadratic or linearity. On each sampling day two sampling vials were injected

206   with 0.5 ppm N_2O standard from the laboratory to ensure the integrity of samples during

207   storage. Samples were analysed for N_2O using an electron capture detector (ECD) at 300°C.

208   A CTC Analytics Combi-pal auto sampler (CTC Analytics, Industriestrasse 20, Zwingen,

209   Switzerland) was used to inject gas samples into the Bruker Gas Chromatograph (Bruker,

210   Bremen, Germany). Evolved N_2O was expressed as parts per million by volume (ppmv)

211   having allowed for ambient concentrations and up-scaled to a flux in g N_2O-N ha^{-1} d^{-1} using

212   the following equation adapted from de Klein and Harvey (2012):

213

214                    $$F_{N2O} = (\partial c/\partial t) * ((M * P)/R * T)) * (V/A)$$

215   Where:

216   ∂c is the change in gas concentration in the chamber headspace during the enclosure period

217   (ppbv), ∂t is the enclosure period expressed in minutes, M is the molar mass of N_2O-N (28 g

218   mol^{-1}), P is atmospheric pressure (Pa) at the time of sampling, T is the temperature (K) at the

219   time of sampling, R is the ideal gas constant (8.314 J k^{-1} mol^{-1}), V is the headspace volume of

220   the chamber and A is the area covered by the chamber (ha).

221   Sampling occurred between 10 am and 2 pm each day as per Chadwick et al. (2014). The

222   limit of detection of the method was calculated by averaging the standard deviation of all

223   ambient samples for each year and then subtracting three standard deviations. This was 0.26

224   ppm and 0.28 ppm for 2013 and 2014, respectively. Anything below this was excluded from

225   the study. In total over the two years 39 data points were removed as limits of detection out

226   of a total of 5980 data points.

227

228   *2.6 Emission Factor calculation*

229   Cumulative N_2O fluxes from each chamber were calculated using trapezoidal integration to

230   interpolate fluxes between sampling dates. Trapezoidal integration was used to linearly

231   integrate fluxes from one sampling day to the next sampling day in order to generate fluxes

232   for 365 days in order to generate cumulative fluxes. For each formulation, cumulative fluxes

233   were calculated using the mean of the five replicates. The EFs were then calculated using the

234   following equation:

235

236   *EF (%) =   N₂O-N cumulative (formulation) – N₂O-N cumulative (unfertilised control) x 100*

$$EF\ (\%) = \frac{N_2O\text{-}N\ cumulative\ (formulation) - N_2O\text{-}N\ cumulative\ (unfertilised\ control)}{Fertiliser\ N\ applied} \times 100$$

237   *Fertiliser N applied*

238

239   Annual EFs were calculated over a 365 day period (IPCC, 2006). As calendar year (January

240   – December) measurement is not appropriate for tillage systems, EFs were calculated from

241   sowing date to the subsequent years sowing date and normalised to 365 days. Nitrous oxide

242   yield efficiency was calculated by dividing the cumulative $N_2O\text{-}N$ ha^{-1} (kg) of a treatment by

243   the grain yield (t ha^{-1}) for the same treatment which produced N_2O yield efficiency (kg N_2O-

244   N t^{-1} grain).

245

246   *2.7 Linearity of N₂O flux*

247   Results from the randomly selected N_2O chambers, used to assess if the N_2O flux was linear,

248   showed on average linear accumulation. Initial analysis of this data was conducted to assess

249   if a flux in N_2O emissions occurred. In some cases there was no flux evident (Table 3). The

250   chambers showing N_2O flux were then analysed for linear or quadratic accumulation of N_2O.

251   Over 90% of these chamber measurements in both sites in both years showed linear

252   accumulation according to the criteria of Chadwick et al. (2014) (Table 3). This shows that

253   the assumption of linear accumulation in the headspace can be used. This is in agreement

254   with work conducted by Chadwick et al. (2014) where over 90% of chamber measurements

255   (n=1970) from multiple field experiments, showed linear N_2O accumulation.

256

257

258   *Table 3.* Linearity samples for 2013 and 2014

	2013	2014
Total No. chambers	260	212
Chambers without N_2O flux	212	73
Chambers with N_2O flux	48	139
Of chambers with flux	**%**	
Quadratic	**8**	**6**
Linear	**92**	**94**

259

260

261   *2.8 Statistical Analysis*

262   Statistical analysis was conducted using the PROC GLIMMIX and PROC MIXED

263   procedures in SAS 9.3 (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.). PROC MIXED

264   was used to conduct a repeated measures analysis of variance (ANOVA) of the temporal N_2O

265   and mineral N data. Residual graphs were generated to check for normality. Log

266   transformation of all temporal data was conducted as there was high variability within the

267   dataset and nonconformity with the assumptions about normality in ANOVA. Residual

268   influence statistics were used to identify potential outliers and showed which data points were

269   the most influential on the entire dataset. These 'potential outliers' were then assessed to

270   check if they were genuine outliers. The assessment of the temporal N_2O data identified only

271   six individual flux measurements that were 'genuine outliers'. These were subsequently

272   removed from the dataset and the average of the other four replicates was then used for that

273   day for gap-filling to generate the cumulative flux. The PROC GLIMMIX procedure was

274   used to test for treatment differences in cumulative emissions. Significant differences were

275   determined according to the F-protected least significant difference test ($p < 0.05$).

276   Dixons test was used to identify outliers in the ambient data. The minimum detectable flux

277   was then calculated according to Appendix 2 in the chamber methodology guidelines (de

278   Klein and Harvey, 2012). Repeatability, standard deviation and repeatability limit was

279   calculated as per (Ellison et al., 2009). The minimum detectable flux (MDF) was calculated

280   to be 2.59 and 7.78 g N_2O-N ha^{-1} day^{-1} in 2013 for small and large chambers, respectively. In

281   2014 the MDF was calculated to be 2.86 and 7.84 g N_2O-N ha^{-1} day^{-1} for small and large

282   chambers, respectively.

283

284   **3 Results**

285   *3.1 Soil and Climatic conditions*

286   The weather during the experiment was typical of the weather for this region with most of the

287   rainfall occurring during the autumn and winter months and the highest temperatures

288   occurring during the summer months (Figure 1a and 2a). In both years, the highest average

289   daily temperature was 17°C in July and the highest total monthly rainfall was in October with

290   189 mm in 2013 and 173mm in 2014. Total monthly rainfall and average temperature were

291   higher in April (68.4mm) and May (74.8mm) in 2014 compared with April and May 2013

292   with 47.2mm and 53.6mm and the 30 year average with 59.1 and 55.7mm for April and May

293   respectively. Water filled pore space ranged from 15.74% - 66.09% in 2013 and 28.6% -

294   68.2% in 2014 with the lowest WFPS% occurring in the summer months. Soil total oxidised

295   nitrogen (TON) and ammonium (NH_4^+) concentrations increased after fertiliser application

296   (Figure 1b and 2b). Elevated soil TON levels occurred following the 2nd split application of

297   CAN. In 2013, levels reached 95.2 mg TON kg^{-1} soil two days post-application and 106.8 mg

298   TON kg^{-1} soil 24 days after application for CAN. After this TON levels from CAN were

299   reduced to below 50 mg TON kg^{-1} soil. In 2014, TON levels from CAN reached 190 mg

300   TON kg^{-1} soil three days after application. Generally, all other fertiliser formulations had

14

301   lower TON levels than CAN. Urea + DCD and urea + NBPT + DCD levels were similar to

302   the unfertilised control levels. The highest NH_4^+ concentration in 2013 was 161.13 mg NH_4^+

303   kg^{-1} soil (urea + NBPT + DCD) and in 2014 was 257.98 mg NH_4^+ kg^{-1} soil (urea + DCD). All

304   fertiliser formulations produced an NH_4^+ peak after application but CAN produced the

305   highest TON peak.

306

307   *3.2 N_2O emissions: fertiliser formulation and N stabilisers at 150 kg N ha^{-1}*

308   Nitrous oxide emissions increased from background levels post-fertiliser application with the

309   highest observed fluxes of 44 g N_2O-N ha^{-1} d^{-1} in 2013 (Figure 1c) and 43g N_2O-N ha^{-1} d^{-1} in

310   2014 (Figure 2c). This peak in N_2O emission corresponded closely with timing of fertiliser

311   application and rainfall occurring 15 and 13 days following the main fertiliser split

312   application in 2013 and 2014 respectively. The association of N_2O emissions with fertiliser

313   application was most pronounced following the second fertiliser application of 120 kg N ha^{-1}.

314   The initial split was 30 kg N ha^{-1} and resulted in a lower quantity of N_2O loss.

315   In 2013 the largest daily fluxes came from urea, CAN and urea + NBPT, in that order. The

316   profile of temporal emissions from urea + DCD and urea + NBPT + DCD were similar to the

317   unfertilised control. Approximately 16 weeks after fertiliser application, emissions returned

318   to background levels (i.e. similar to that of the unfertilised control) and remained so for the

319   remainder of the year in 2013 for all formulations.

320   In 2014 there was a peak in emissions after fertiliser application with the largest daily fluxes

321   from CAN, urea + NBPT and urea in that order. Approximately four to six weeks after the

322   second split fertiliser application emissions returned to background levels and remained so

323   for the remainder of the year for all formulations.

324

325

326   *3.3 Cumulative emissions and emission factors*

327   Cumulative N_2O emissions were all below 0.5% across all formulations and years. In both

328   years CAN produced significantly higher emissions than the unfertilised control with 1161 g

329   N_2O-N ha^{-1} in 2013 and 513 g N_2O-N ha^{-1} in 2014 (Table 4) compared with 424 g N_2O-N ha^{-1}

330   from the control in 2013 and 191 g N_2O-N ha^{-1} from the control in 2014. In 2013 N_2O loss

331   from CAN, urea, urea + DCD was not significantly different. Urea + NBPT and urea + NBPT

332   + DCD had significantly lower emissions compared to CAN and were also not significantly

333   different to N_2O emissions from the unfertilised control. In 2014 urea + DCD was the sole

334   fertiliser formulation which had significantly lower N_2O loss compared to CAN, urea and

335   urea + MICO. EFs ranged from 0 – 0.49% with the numerically highest EF of 0.49% from

336   CAN in 2013. CAN and urea had the highest direct EFs in each year and all EFs were lower

337   than the IPCC default of 1% regardless of formulation. Urea + NBPT + DCD had the lowest

338   EF in 2013 and urea + DCD had the lowest EF in 2014 and the lowest mean EF.

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351   ***Table 4.*** Cumulative direct N_2O emissions in g N_2O-N ha^{-1} and emission factors for 2013 and

352   2014

Fertiliser Formulation	2013		2014		Average
	Cumulative Emissions g N$_2$O-N ha^{-1}	Emission Factor (%)	Cumulative Emissions g N$_2$O-N ha^{-1}	Emission Factor (%)	Emission Factor (%)
CAN	1161a (166)	0.49	513a (94)	0.21	0.35
Urea	889ab (45)	0.31	538a (99)	0.23	0.27
Urea + NBPT	772bc (173)	0.23	427ab (41)	0.16	0.20
Urea + DCD	804ab (140)	0.25	191b (62)	0	0.13
Urea + NBPT + DCD	723bc (105)	0.20	364ab (105)	0.12	0.16
Urea + MICO	N/A N/A		455a (176)	0.18	0.18
Control	423c (57)		191b (95)		

353   *Different letters represent significant differences between treatments for cumulative emissions using F protected LSD test

354   ($P<0.05$) and comparisons are within each year

355   *Treatment SE (standard error) for each treatment at each site shown in brackets.

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361 *3.4 Impact of fertiliser rate on N_2O emissions*

362 The impact of N rate (100-200 kg N ha^{-1}) on EF$_1$ was unclear. There was no significant

363 impact of application rate on the CAN EF in either year as evidenced by the lack of a

364 significant correlation between the EF and N rate (Table 5). However, a significant negative

365 correlation between N rate and the urea EF was observed in 2013 but not in 2014 (Table 5).

366 The model that best fitted this equation was quadratic with an r^2 value of 0.96; the equation of

367 the line is presented in Table 5.

368

369 ***Table 5.*** Effect of N rate on N_2O emission factors for CAN and Urea

Treatment	P value (slope different to zero)	Equation*
CAN 2013	0.258	N/A
Urea 2013	0.0321	$y = 8E\text{-}05x^2 - 0.0287x + 2.8594$
CAN 2014	0.225	N/A
Urea 2014	0.0811	N/A

370 *y = Emission factor and x = N fertiliser rate

371

372 *3.5 N_2O yield efficiency*

373 Nitrous oxide yield efficiency ranged from 0.09 – 0.16 kg N_2O-N t^{-1} grain in 2013 and 0.02 –

374 0.07 kg N_2O-N t^{-1} grain in 2014. There were no significant differences between fertiliser

375 formulations in either year but there were differences between the unfertilised control and

376 fertiliser treatments (Figure 3). In 2013, the unfertilised control was significantly higher than

377 all fertiliser treatments with 0.16 kg N_2O-N t^{-1} grain except for CAN and in 2014 the

378 unfertilised control was higher than urea + DCD with 0.05 kg N_2O-N t^{-1} grain and not

379 different to any other treatment.

380 **4 Discussion**

381 *4.1 Effect of environmental factors on N_2O emissions*

382 The application of N resulted in a peak in soil mineral N concentrations with CAN producing

383 significantly higher NO_3^- peaks compared to other N forms and all fertiliser formulations

384 producing NH_4^+ peaks. This study showed that using a urea based fertiliser reduced the soil

385 NO_3^- pool compared to CAN. Thus, there is less TON for denitrification and leaching from

386 the urea based fertilisers. The soil NH_4^+ pool was similar regardless of the N formulation

387 used.

388 Whilst rainfall and temperature at the time of fertiliser application were higher in 2014 than

389 in 2013, cumulative emissions were lower in 2014 compared with 2013. In 2013 there were

390 multiple emission peaks resulting in higher cumulative emissions whereas in 2014 there was

391 one main peak after each fertiliser application. The slightly lower levels of N_2O in 2014 could

392 indicate that either complete denitrification occurred producing N_2 instead of N_2O (Focht et

393 al., 1979), NO_3^- or that the nitrate was leached due to higher rainfall events combined with

394 the free-draining soil texture, or that more N was taken up by the crop due to less drought

395 stress.

396 In general, cumulative emissions were low ranging from 191 g N_2O-N ha^{-1} yr^{-1} to 1161 g

397 N_2O-N ha^{-1} yr^{-1} and with EF_1 ranging from 0 to 0.49%. This is consistent with previous

398 studies on spring barley sites in Ireland, where EF for CAN during the growing season (not

399 full year) was observed to be 0.5% (Abdalla et al., 2010). The relatively low EF_1 could be

400 explained, in part, by the soil characteristics. The soil was a free-draining cambisol with a C

401 content of 2.88%, which is typical of Irish arable soils. In a meta-analysis of over 1000

402 studies, Stehfest and Bouwman (2006) concluded that N_2O emissions were significantly

403 lower on soils with SOC <3%   and Gilsanz et al (2016) observed the lowest EFs in soil

404 textures with low clay content (less than 50%) and with sand content greater than 50%. In a

405 study at three arable sites, the EF_1 for ammonium nitrate was observed to be substantially

406 lower than the default value (0.2% and 0.33%) at two free-draining sites (Bell et al., 2015). In

407 contrast, grasslands exhibit both higher mean emissions and a larger range in EFs (Harty et

408 al., 2016). Dobbie and Smith (2003a) reported EF_1 ranging from 1%-3% in Scottish

409 grasslands whilst previous studies on total N_2O losses in Irish grasslands (including N

410 deposition form fertiliser (EF_1) and animal excreta (EF_3)) have exhibited a range from 0.7%

411 to 7.7% (Hyde et al., 2006; Rafique et al., 2011; Li et al., 2011, Burchill et al., 2014).

412

413 *4.2 Effect of fertiliser formulation and incorporation of N stabilisers on N_2O emissions*

414 N_2O emission peaks in general corresponded with rainfall events and elevated soil TON and

415 NH_4^+ concentrations. The majority of N_2O emissions occurred after the second and the larger

416 split fertiliser application with the highest N_2O emissions and EFs associated with CAN and

417 urea application. There were no significant differences in N_2O emissions between CAN and

418 urea. A comparison between urea and ammonium nitrate (AN) at three UK sites also found

419 no differences in N_2O emissions between fertiliser formulations, with higher emissions for

420 both fertilisers at the site with highest rainfall (Bell et al., 2015). Similarly, Louro et al.

421 (2015) reported no significant fertiliser formulation effect on N_2O emissions. In contrast,

422 Dobbie and Smith (2003a) observed lower N_2O emissions associated with urea application

423 compared to ammonium nitrate (AN). This effect was season dependant with no differences

424 when fertiliser was applied in late summer. The findings from this study suggest that the

425 addition of the nitrification inhibitor DCD to urea has potential to reduce N_2O emissions by

426 30% compared to CAN. The inhibitory effect of DCD can vary depending on climate and soil

427 conditions as well as vegetation type (Gilsanz et al., 2016) and is likely to be more effective

428 where there are higher losses such as wetter soils. Bell et al. (2015) observed a decrease in

429 the EF_1 for AN from 0.55% to 0.06% upon application of DCD. In addition, Dobbie and

430   Smith (2003a) observed a 50% reduction in cumulative emissions using urea + DCD

431   compared to urea alone, but observed no benefit of urea + NBPT on direct N_2O emissions.

432   The potential effects of DCD uptake by the plant and contamination in crop off takes is

433   needed as recently highlighted in New Zealand (Pal et al., 2016). In studies with higher

434   emissions the inclusion of a urease inhibitor with urea reduced N_2O emissions compared with

435   CAN (McTaggart et al., 1997). While NBPT treated urea did not reduce direct N_2O emissions

436   compared to urea in this study, inclusion of NBPT with urea has been shown to reduce

437   volatilisation from urea (Watson et al., 2009; Forrestal et al., 2015) which will reduce indirect

438   N_2O emission associated with the deposition of atmospheric NH_3 (Asman et al., 1998). Urea

439   + MICO showed no effect on N_2O emissions compared to CAN or urea. This corresponds

440   with the literature which shows that urea + MICO is not an effective nitrification or urease

441   inhibitor (Chien et al., 2014;Franzen et al., 2011., Goos, 2013). The EFs for all fertiliser

442   formulations were <50% of the IPCC default value of 1%. Against this background these

443   fertiliser formulations appear to have similar N_2O loss potential in spring barley which tends

444   to be cropped to free draining sites similar to this study. Other studies on arable land in

445   similar climates have also shown EFs lower than the IPCC default (Bell et al., 2015; Abdalla

446   et al., 2010).

447   The N_2O yield efficiency was highest for the unfertilised control but there were no

448   differences between fertiliser formulations which is in agreement with Hinton et al (2015).

449   It's important to account for crop yield as well as N_2O emissions when assessing fertiliser

450   formulations to determine if they are economically viable (Hinton et al., 2015). This study

451   showed similar N_2O yield efficiency regardless of the fertiliser formulation used.

452

453

454

455   *4.3 Effect of N rate on N$_2$O emissions*

456   There was no EF response to rate of N application for CAN and urea in 2014. Bell et al

457   (2015) also observed no consistent increase in EF$_1$ in response to increased rate of AN

458   applied to arable cropped soils. In the current study there was a negative correlation observed

459   between EF$_1$ and rate of urea application 2014, with EF$_1$ 0.7% at the lowest N application

460   (100 kg N ha^{-1}) compared to 0.4% at the highest N application (200 kg N ha^{-1}). This may be

461   related to higher ammonia volatilisation occurring at higher N fertiliser application rates

462   (Black et al., 1985; Van der Weerden and Jarvis, 1997). The negative or lack of correlation

463   between EF$_1$ and applied N rate in the present study indicates that higher NH$_3$ loss may have

464   taken place and this could result in reduced yields which has been observed in previous

465   studies (Conry et al., 1997; Gately, 1994; Devine and Holmes, 1963). The addition of NBPT

466   protects against this NH$_3$ loss with reductions of 78.5% on average measured in Irish

467   grassland (Forrestal et al., 2015).

468

469   *4.5 Emission Factors and comparison to IPCC default*

470   Over the two year period of the study the EFs from all fertiliser formulations ranged from 0%

471   (from urea + DCD in 2014) - 0.49% (from CAN in 2013). Other studies on UK soils have

472   shown higher EFs from AN than those observed from CAN in this study (Hinton et al., 2015;

473   Dobbie et al., 1999). The fact that the highest EF recorded (0.49%) was half the magnitude of

474   the IPCC 1% default, highlights the potential importance of countries moving to a tier 2

475   methodology using system specific data to generate more accurate N$_2$O emission inventories.

476   Further research is required in order to determine the appropriateness of the use of the default

477   EF in other scenarios such as different land use types. Furthermore the use of nitrification

478   inhibitors significantly decreased the observed EF. While the use of urease inhibitors did not

479   lead to significant reductions in direct N$_2$O EFs, potential reductions in ammonia

480 volatilisation as a result of urease inhibition could significantly reduce indirect N_2O losses

481 associated with the redeposition of atmospheric ammonia (EF_4).

482

5 Conclusions

484 Overall, N_2O emissions from the fertilisers tested in this study were less than half the IPPC

485 default value of 1%. The lack of a clear relationship between fertiliser rate and direct N_2O

486 emissions questions the appropriateness of the IPCC default values on soils with low

487 emissions in temperate conditions. This site is representative of the soil type for the majority

488 of spring barley in Ireland and so, based on this study, it is likely that N_2O emissions from the

489 majority of spring barley in Ireland are below the IPCC default value. In terms of fertiliser

490 form, it is important to account for indirect emissions from NH_3 volatilisation when

491 calculating EFs upon switching from ammonium nitrate to urea-based fertiliser forms, as

492 otherwise total emissions associated with N application will be underestimated. The present

493 research emphasises the importance of developing country and system specific emission

494 factors to better estimate greenhouse gas emissions from agriculture.

495

503

504 **Figure 1.** 2013 temporal emissions data (a) daily total rainfall (mm) and daily average

505 temperature (°C) and, (b) daily soil mineral N concentrations (0–10 cm). (c) daily N_2O

506 emissions in g N_2O-N ha^{-1} day^{-1} *arrows represent fertiliser application

507

508 **Figure 2.** temporal emissions data (a) daily total rainfall (mm) and daily average temperature

509 (°C) and, (b) daily soil mineral N concentrations (0–10 cm). (c) daily N_2O emissions in g

510 N_2O-N ha^{-1} day^{-1} *arrows represent fertiliser application

511

512 **Figure 3.** N_2O yield efficiency (kg N_2O-N t^{-1} grain) for 2013 and 2014 *Different letters

513 represent significant differences between treatments using F protected LSD test ($P<0.05$) and

514 comparisons are within each year

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