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Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated Cambisol in Scotland

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1 **Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities**

2 **from a cultivated Cambisol in Scotland**

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1. Introduction

Nitrous oxide (N_2O) is a powerful greenhouse gas (GHG) which accounts for 8 % of total global GHG emissions (Reay et al., 2012) and has a global warming potential 298 times greater than that of CO_2 (Forster et al., 2007). The breakdown of N_2O to NO in the stratosphere also results in the depletion of stratospheric ozone (Crutzen and Lelieveld, 2001). Although N_2O is a naturally occurring gas, there has been an increase in atmospheric concentration of 16 % since 1750 which is primarily attributed to emissions from fertilized agricultural soils (Davidson, 2009). Global annual emissions from agricultural soils are currently estimated to be around 4 Tg N_2O-N (Reay et al., 2012).

The production of N_2O by fertilised arable soils is associated with the application of inorganic N fertilisers and manures or soil disturbance, which cause an increase in soil concentrations of ammonium (NH_4^+) and nitrate (NO_3^-); which is responsible for the subsequent production of N_2O as a byproduct of the microbial processes of nitrification and denitrification (Chapuis-Lardy et al., 2007; Inselbacher et al., 2011). Emissions from fertilised soils have high spatial and temporal variability (Flechard et al., 2007; Lilly et al., 2003) due to the influence of multiple factors such as soil water filled pore space (WFPS), soil compaction, pH and temperature on the N_2O source processes (Bessou et al., 2010; Castellano et al., 2010; Pierzynski et al., 2005; Smith et al., 2003). The high spatial and temporal variability of N_2O emissions from agricultural soils

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41   makes it difficult to accurately assess annual fluxes. It has been suggested that a solution to this

42   problem is the use of high frequency long path length measurement techniques such as eddy

43   covariance (Flechard et al., 2007). However, such methods require large areas and are typically

44   of limited value in plot based field experiments where manipulation treatments are compared,

45   and emission factors (EFs) need to be calculated (as an unfertilised control area is needed too).

46   An alternative approach, used in this study, is the use of static chambers with high temporal and

47   spatial replication (Chadwick et al., 2014). Previous studies of N_2O emissions from agricultural

48   soils using the static closed chamber technique often involved the use of only a small number of

49   replicate chambers per treatment and a low sampling frequency over a short period of time. For

50   example, a number of studies have used six or less static chambers per treatment (Ball et al.,

51   1999; Clayton et al., 1997; Dobbie et al., 1999; Dobbie and Smith, 2003; Smith et al., 2012).

52   Previous studies have also often been based on short measurement periods ranging from 5 days

53   to 6 weeks after fertiliser application (Skiba and Ball, 2002; Skiba et al., 2002; Smith et al.,

54   2012). Furthermore, previous studies have not always adequately captured temporal dynamics

55   where gas samples were taken at intervals of 2-4 weeks (Rees et al., 2013).

56   The relationship between the amount of N fertiliser applied and the magnitude of N_2O emissions

57   is quantified through the use of an EF (EF1) which expresses the quantity of N_2O-N emitted as a

58   proportion of the N fertiliser applied. The EF calculation also accounts for background emissions

59   which are largely due to mineralisation of crop residues (IPCC, 2006). Bouwman (1996)

60   reviewed experiments of at least a year in length and recommended an EF (EF1) of 1.25 % of the

61   N applied to express the relationship between applied N fertiliser and N_2O emissions. The IPCC

62   subsequently used this as a "default EF" to enable calculation of countries' N_2O emissions from

63   soils receiving inorganic fertiliser N (IPCC, 1996). This value has since been revised downwards

64   on the basis of more recent evidence to give an EF of 1 % of N applied for use in the Tier 1

65   methodology for calculating N_2O emissions (IPCC, 2006). However many countries including

66   the UK have not yet adopted the 1 % EF in their national inventory calculations. This default EF

67   attempts to estimate typical emissions across large spatial areas and time periods, however there

68   is concern that local soil and climatic conditions, and the type and rate of fertiliser used can lead

69   to significant variance from average conditions (Smith et al., 2012). The use of a 1.25 % EF has

70   been controversial in Scotland where it has been demonstrated that large changes in soil WFPS

71   may result in Scottish EFs which are atypical of the whole of the UK (Dobbie et al., 1999;

72   Dobbie and Smith, 2003). This is reflected in calculated N_2O EFs ranging from 0.17 – 7 % for a

73   range of N sources for Scottish agricultural soils (Clayton et al., 1997; Dobbie et al., 1999; Smith

74   et al., 1998a). To improve the accuracy of agricultural N_2O reporting it is necessary for

75   investigation into the effects of controlling variables on N_2O emissions and the appropriateness

76   of utilising a 1.25 % EF, or the new 1 % EF, regardless of location, and this is particularly

77   relevant in areas of the UK which may experience extreme or unusual climatic conditions.

78

79   Mitigation of agricultural N_2O emissions is necessary if we are to limit the contribution of

80   agriculture to climate change. The use of nitrification inhibitors (NIs) such as dicyandiamide

81   (DCD) which act to decrease N_2O emissions by deactivating the ammonia monooxygenase

82   enzyme used in the primary stage of nitrification (Amberger, 1989) have proved successful in

83   mitigating agricultural N_2O emissions (Di and Cameron, 2003; Di et al., 2007) and have also

84   demonstrated the potential to increase crop yields (Abalos et al., 2014). However, there has been

85   little investigation into the effectiveness of DCD in UK agricultural systems and more research

86   in this area is required. Another N_2O mitigation option which requires further investigation is the

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87   use of split applications of N fertiliser. Split applications result in the application of smaller

88   individual doses of fertiliser, which reduces surplus N in the soil and decreases the potential for

89   loss of N via transformation to N_2O or leaching, in addition to being more suitable for crop

90   requirements (Burton et al., 2008), potentially increasing the nitrogen use efficiency of fertilisers.

91   Reducing the amount of surplus N is an important method of decreasing N_2O emissions as it not

92   only has positive impacts on the environment but is also financially beneficial for the farmer.

93   Altering the amount or type of fertiliser applied is another means by which surplus N may be

94   decreased, and research has indicated that the use of urea rather than ammonium nitrate (AN)

95   fertiliser may result in lower N_2O emissions (Dobbie and Smith, 2003; Smith et al., 2012).

96   Although it is important to minimise N_2O emissions from agricultural soils, it will also be

97   necessary in the future to produce greater quantities of food, meaning that crop yield must not be

98   negatively impacted by mitigation options. Emission intensities i.e. the amount of N_2O produced

99   per unit of crop yield, are therefore a vital indicator of the potential of any N_2O mitigation option

100   (Van Groenigen et al., 2010), although research into this area has thus far been limited.

101   This work forms part of a nationwide project to assess the effect of a range of organic and

102   inorganic nitrogen fertiliser treatments on N_2O emissions from agricultural soils with the results

103   being used to improve agricultural management systems and to reduce uncertainty in the UK

104   agricultural greenhouse gas inventory (GHG, 2013). More specifically, the aims are to:

105   i). Compare N_2O emissions, calculated EFs and emission intensities from different inorganic

106   fertiliser treatments

107   ii). Investigate the efficacy of potential N_2O mitigation options.

108   iii). Assess the appropriateness of the use of the standard 1.25 % or 1 % EF for the area under

109   investigation.

110   **2. Materials and Methods**

111   *2.1   Site description*

112   The experiment began in April 2011 at Gilchriston in south east Scotland (Grid reference:

113   NT479658). Gilchriston is a commercial arable farm, selected for its location in one of the

114   principal geoclimatic zones which support arable production in the UK. The site characteristics

115   are described in Table 1. Soil pH, organic matter and bulk density were calculated using field

116   measurements, other soil information was obtained from Hipkin (1989).

117   *2.2   Experimental design*

118   Nitrogen fertiliser treatments were compared that ranged from a control (0 kg N ha^{-1}) to 200 kg

119   N ha^{-1} and included the recommended application rate for the area of 120 kg N ha^{-1} (Defra,

120   2010). The fertiliser was applied either in the form of ammonium nitrate (AN) or urea. Fertiliser

121   was applied in two doses (three doses for one treatment) in April and May 2011, by hand to the

122   entire plot, to simulate agronomic practice. The NI DCD was applied at a rate of 10 kg ha^{-1} as a

123   spray an hour after the application of AN and urea. Further details of treatments are presented in

124   Table 2. The experimental layout consisted of 10 m x 3 m plots replicated three times for each

125   treatment in a randomized block design. For the duration of the experiment, pesticides were

126   applied according to standard recommendations, and P_2O_5 and K_2O were applied to all plots at

127   rates of 60 kg ha^{-1} and 90 kg ha^{-1}, respectively, in order to satisfy crop demand.

128   *2.3   Gas and soil sampling, measurements and analysis*

129   Nitrous oxide fluxes were measured at the experimental site over a one year period (7th April

130   2011 – 30th March 2012) using the static closed chamber technique (Chadwick et al., 2014;

131   Clayton et al., 1994) and with a methodology that was consistent with Global Research Alliance

132   guidelines (de Kleine and Harvey, 2012). Although the N_2O results are referred to as "annual"

133   emissions, the precise number of days this period represents is 358 days. The intense N_2O

134   sampling frequency was based on the assumption that most of the total direct N_2O emissions

135   occur within the first month following each dose of fertiliser application (Dobbie et al., 1999).

136   The sampling strategy therefore involved around 50 % of the total N_2O measurements occurring

137   during this period of expected high emissions in order to capture the variations between

138   treatments.

139

140   Five circular chambers made of opaque polypropylene (200 mm diameter, 300 mm height and

141   soil surface area coverage of approximately 0.126 m²) were installed per plot, resulting in the use

142   of 15 chambers per treatment. Chambers were installed by cutting a 5 cm deep slot into the soil

143   and inserting the base of the chamber into this slot. Soil was tightly packed around the base of

144   the chamber (on the outside) to ensure a good seal. The chambers were left in place for the whole

145   experiment except when agricultural operations such as harvest deemed removal necessary.

146   Extensions were added to the tops of the chambers during the growing season in order to avoid

147   damaging the plants within the chambers. On each sampling occasion, aluminium lids were

148   clipped onto the top of each chamber and the chamber remained covered for 40 minutes. The

149   headspace was then sampled through a small sampling port in the lid using a syringe and gas

150   samples were transferred to pre-evacuated 20-22 ml glass vials. Ambient and 'linearity check'

151   gas samples were also collected. The linearity check involved collecting samples at 10 minute

152   intervals from 3 randomly selected chambers (1 from each block) throughout the sampling

153   period. Sampling was conducted between 10:00 and 12:00 h to ensure consistency. See

154   Chadwick et al. (2014) for further methodology information.

155

156   Gas samples were analysed for N_2O concentrations using an Agilent 7890A Gas Chromatograph

157   (GC) fitted with an electron capture detector (Agilent Technologies, Berkshire, UK) and a CTC

158   Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK). The GC response was

159   calibrated using certified N_2O gas standards (0.35, 1.1, 5.1, 10.7 ppm) and the N_2O limit of

160   detection was 0.025ppm. Air temperature was recorded on every N_2O sampling occasion and

161   chamber height was also measured for use in N_2O flux calculations. Daily N_2O fluxes were

162   calculated using linear regression which assumes a linear increase in N_2O concentration in a

163   known volume over a known period of time, and the ideal gas law (Saggar et al., 2008).

164   Cumulative N_2O fluxes from each chamber were calculated using the trapezoidal rule (area

165   under the curve) to interpolate fluxes between sampling points. For each treatment, cumulative

166   fluxes were calculated using the mean of the 5 chambers per plot, in order to calculate a

167   treatment mean cumulative emission value and associated standard error.

168

169   Composite soil samples consisting of five cores (0-10 cm depth) collected at random locations

170   using a 30 mm diameter auger were taken from each block on each N_2O sampling occasion for

171   soil gravimetric water content (GWC) determination, i.e. one soil moisture content measurement

172   per block on each occasion. Composite soil samples from each plot were also collected in this

173   way at approximately monthly intervals throughout the one-year experiment for soil mineral N

174   content determination, i.e. generating one sample per plot. Fresh soil samples were sieved

175 (<4mm) and extracted using 2M KCl (soil to extractant ratio 1:2) for determination of soil

176 ammonium (NH_4^+-N) and nitrate (NO_3^--N) contents using a Skalar San^{++} continuous flow

177 autoanalyser (Skalar, York, UK). Soil bulk density was determined for each block through

178 collection of intact soil samples using metal rings on frequent occasions throughout the

179 experiment. Soil bulk density and GWC were used to calculate soil WFPS (%) on each gas

180 sampling occasion (Robertson, 1999).

181 A meteorological station at the site recorded daily rainfall. Air and 10-cm depth soil

182 temperatures were also recorded using a temperature probe (RS Components, Northamptonshire,

183 UK) on each N_2O sampling occasion.

184 The crop was harvested on 22nd August 2011 using a small plot harvester which harvested an

185 area of 15m^2 from each plot. Just prior to harvest, a random sample of 100 tillers per plot was

186 also collected by hand. This was threshed and weighed to determine the ratio of grain to straw

187 and chaff. The % dry matter and N content of the grain, and the mixed straw and chaff, from

188 each plot was determined.

189   *2.4 Emission Factor calculation*

190 Emission factors, which express the N_2O-N emitted from each treatment as a percentage of the

191 total N applied, were calculated (subtracting control values from each of the 3 blocks from

192 corresponding treatment values as appropriate before calculating mean treatment EFs) using the

193 following equation:

$$EF = \left(\frac{Cumulative\ annual\ N_2O flux\ (kg\ N_2O\text{-}N) - cumulative\ annual\ N_2O\ flux\ from\ control\ (kg\ N_2O\text{-}N)}{N\ applied\ (kgN)} \right) \times 100$$

194   EFs were calculated for three separate timescales: 1). An annual EF was calculated as

195   recommended by Bouwman (1996). 2). A "seasonal" EF was calculated which included N_2O

196   data up until harvest to take into account the effects of crop growth on N_2O emissions and the

197   time taken for soil mineral N levels to return to "background" levels. 3). A "five week" EF was

198   calculated for the 5 weeks following the first fertiliser application. This time scale was chosen as

199   it has been reported that the majority of emissions take place during the 4 weeks following

200   fertiliser application (Dobbie et al., 1999) and would therefore enable clearer identification of

201   treatment effects. However, due to dry weather during this period there were very low N_2O

202   emissions from all treatments, so it was extended to 5 weeks to include the large peak in

203   emissions which occurred during May.

204

205   *2.5 Statistical analysis*

206   Statistical data analyses were carried out using Genstat (16.1). The occurrence of any significant

207   differences in measurements between treatments was tested using one-way analysis of variance

208   (ANOVA) with blocks. Data were checked for normality before ANOVAs were applied and

209   analysis of residuals was used to determine outliers. Two outliers were identified during the

210   analysis of the cumulative N_2O data and the annual and seasonal EFs, these were from blocks 2

211   and 3 of the AN 40 treatment. These outliers were subsequently excluded from the analysis.

212   Treatment effects were deemed significant if $p \leq 0.05$. Regression analysis was performed to

213   determine the relationship between nitrogen applied and the cumulative annual emission. The

214   REML procedure was used for this analysis with nitrogen level, specified as a variate, as the

215   fixed factor, and the block was specified as the random factor. REML regression was also used

216   to analyse the relationship between the daily N_2O emissions and the % WFPS with the block

217   specified as the random factor. In this case, the emissions were transformed using natural

218   logarithms. Due to large negative emissions, 25 g N_2O-N ha^{-1} d^{-1} was added to the emissions

219   before transformation. On analysis of the residual plots, one outlier was identified and removed

220   from the analysis (Block 2 on 7th July).

221

222   **3. Results**

223   *3.1 Nitrous oxide fluxes*

224   Nitrous oxide fluxes showed high temporal variation with most emissions occurring during a few

225   intermittent flux episodes, and also varied widely between treatments (Figure 2). Emission

226   maxima of 170-190 g N_2O-N ha^{-1} d^{-1} from the AN 160 and AN 200 treatments occurred 13 days

227   after the second fertiliser application in May 2011. Total N_2O emissions were higher in August

228   than any other month with a maximum cumulative monthly value of 0.013 kg N_2O ha^{-1} from the

229   CON treatment. Negative N_2O fluxes were occasionally observed during the experimental period

230   with the largest negative flux of -18 g N_2O-N ha^{-1} d^{-1} occurring for the AN 80 and urea 120 + NI

231   treatments in July.

232   Cumulative N_2O emissions for the one year study period showed marked treatment effects

233   (Figure 3), with a general increase in cumulative N_2O emissions associated with larger N

234   applications. During the 1 way ANOVA with blocks, 2 outliers were observed from the analysis

235   of the residuals. These were the cumulative emissions from blocks 2 and 3 of the AN 40

236   treatment and these were subsequently removed from the analysis. Maximum cumulative

237   emissions were recorded from the AN 200 treatment with a value of 3.82 kg N_2O ha^{-}

238    $^{1.}$ Cumulative emissions from the AN 200 treatment were significantly higher (p=0.009. SED =

239   0.605) than from the CON, urea 120, urea 120 + NI, AN 120 + NI, AN 40 and AN 80 treatments.

240   The lowest cumulative N_2O emissions were from the Urea 120 + NI treatment with a value of

241   1.32 kg N_2O ha^{-1}. This was a non significant 45 % reduction in cumulative emissions in

242   comparison to the urea 120 treatment. There was a significant 38 % decrease in cumulative

243   emissions from the AN 120 + NI treatment in comparison to the AN 120 treatment; however

244   there was no significant difference between the AN 120 + NI and that AN (3 splits) . Cumulative

245   N_2O emissions from the AN (3 splits) and urea 120 treatments showed a trend for lower

246   emissions than from the AN 120 treatment by 11 % and 26 %.

247

248   *3.2 Environmental conditions*

249   The weather during the experimental period was atypical for this region, with a dry spring,

250   followed by an unusually wet summer which coincided with low temperatures (Figure 1a and b).

251   The high N_2O emissions observed during the summer corresponded with the occurrence of most

252   of the large rainfall events during this period (Figures 1 and 2). The May emission peak occurred

253   in a relatively dry period (the soil WFPS was 38 %) but during the peak in emissions in August

254   the soil was considerably wetter (soil WFPS values of ~50 %). Despite the high rainfall, only 4

255   % of the measurement days had 50-70 % WFPS with all of the remaining days having < 50 %

256   WFPS. A WFPS value of >60-70 % is generally associated with denitrification conditions, and

257   hence with greater N_2O fluxes (Davidson, 1991).

258   *3.3 Emission factors*

259   Emission factors for each time period (annual, seasonal and 5 weeks) were calculated (Table 2).

260   The maximum annual EF was 1.35 from the AN 120 treatment and the mean annual EF was

261 0.69, in comparison to the mean seasonal EF of 0.40 and the mean 5 week EF of 0.44. Two

262 negative EFs were obtained for the annual and seasonal urea 120 + NI treatment. These represent

263 positive emissions which are lower than the unfertilised control due to the EF calculation method

264 used, in which control fluxes are subtracted from treatment fluxes. There were no significant

265 differences between EFs for all treatments at any of the three timescales (EF annual, p=0.082; EF

266 seasonal, p= 0.082; EF 5 wk, p = 0.209).

267   *3.4 Soil mineral N*

268 Soil NO_3^--N and NH_4^+-N concentrations increased following fertiliser application with a peak in

269 NO_3^--N concentration of 68 kg N ha^{-1} in the AN 200 treatment and a peak in NH_4^+-N

270 concentration of 57 kg N ha^{-1} in the urea 120 + NI treatment, just over a month after the final

271 fertiliser application (Figure 4). As expected the mineral N concentrations increased as the

272 application rate of AN fertiliser increased. The NI treatments acted to significantly increase

273 NH_4^+-N concentrations (p< 0.05) and significantly decrease NO_3^--N concentrations (p<0.05) in

274 comparison to the non-NI amended treatments. Following peak soil NO_3^--N and NH_4^+-N

275 concentrations, values decreased to < 5 kg N ha^1. The concentrations of both NO_3^--N and NH_4^+-

276 N were consistently below 5 kg N ha^{-1} in the period between August 2011-March 2012.

277

278   *3.5 Crop yield and yield scaled emissions*

279 Crop yield (grain harvest at 15 % dry matter) ranged from a minimum of 1.46 t ha^{-1} for the

280 control treatment to 9.30 t ha^{-1} for the AN 200 treatment (Figure 5a). Significantly greater crop

281 yield was obtained from the AN 160 and AN 200 treatments (p<0.001, SED = 0.1682) than

282 from all other treatments. The crop yield obtained was dependent on the amount of N fertiliser

283   applied, with greater crop yield obtained for larger applications of N fertiliser. Crop yield was

284   significantly decreased by 9 % and 10 %, respectively for the AN 120 + NI and the urea 120 +

285   NI treatments in comparison to their non NI amended counterparts and there was significantly

286   lower crop yield from the AN (3 splits) treatment in comparison to the AN 120 treatment. Yield

287   scaled emissions generally decreased with increasing rates of N fertiliser application from a

288   maximum of 1.15 kg N_2O ton^{-1} grain for the control treatment, to a minimum of 0.18 kg N_2O

289   ton^{-1} grain for the urea 120 + NI treatment (Figure 5b). There was a significant effect of

290   treatment on yield scaled emissions (p=0.002, SED=0.1742) which showed that the control

291   treatment had significantly higher emission intensities than the fertiliser treatments.

292   **4. Discussion**

293   *4.1 Linearity of N_2O emissions with N application*

294   This study demonstrated the value of a high intensity sampling strategy in assessing variability in

295   N_2O emissions between fertiliser treatments. Greater applications of N fertiliser generally

296   resulted in higher cumulative N_2O emissions due to the increase in soil NO_3^- and NH_4^+ contents.

297   There was a strong linear relationship (p<0.001) between the amount of N fertiliser applied and

298   the magnitude of the cumulative N_2O emissions (Figure 6). Treatments AN 80 and AN 120

299   demonstrated smaller variability in N_2O emissions between blocks in comparison to the other

300   treatments. The IPCC Tier 1 EF approach assumes that N_2O emissions are a linear function of N

301   application (Philibert et al., 2012) and our results support this assumption, in contrast to some

302   suggestions that the relationship between N input and N_2O emissions may be non-linear (Hoben

303   et al., 2011; McSwiney and Robertson, 2005).

304

4.2 Cumulative N$_2$O emissions and environmental controls

306   Cumulative annual emissions from all treatments were particularly high in comparison to

307   comparable experiments in this area. McTaggart et al. (1997) and Smith et al. (1998a) measured

308   N$_2$O emissions from spring barley crops fertilised with 120 kg N ha^{-1} in South East Scotland in

309   1993 and 1994-1995 respectively and reported emissions of 0.8 kg N$_2$O-N ha^{-1}, considerably

310   lower than the 3.28 kg N$_2$O-N ha^{-1} reported for the AN 120 treatment from our experiment. The

311   lower frequency of measurements carried out by McTaggart et al. (1997) and Smith et al.

312   (1998a) may explain their reported lower emissions. The high emissions observed during this

313   experiment contrasts with work by Smith et al. (1998a), which reported that emissions from

314   Scottish sites were generally small due to low spring and summer temperatures which reduces

315   the production of N$_2$O. Most of the N$_2$O emissions are expected to occur in the four weeks

316   following fertiliser application (Bouwman, 1996) and the mean soil temperature recorded during

317   this period for our experiment was 13.3 °C, only 0.6 °C lower than the maximum mean monthly

318   soil temperature observed in July which will have promoted high N$_2$O production.

319   Previous work by Dobbie et al. (1999), Flechard et al. (2007), Jones (2007) and Rees et al.

320   (2013) has demonstrated that the key factors affecting N$_2$O emissions from N fertilised

321   agricultural soils are % soil WFPS, soil temperature and soil mineral N. However, there are

322   threshold levels of these factors and if this threshold is not exceeded by any of these variables

323   then N$_2$O production may be limited (Dobbie and Smith, 2003; Topp et al., 2013). During the

324   period immediately following fertiliser application and the subsequent summer months when soil

325   mineral N contents and temperature were not limiting to N$_2$O production, the primary variable

326   affecting emissions was % soil WFPS . This limiting effect was clearly demonstrated in this

327   experiment in the period between the first fertiliser application and the large peak in emissions

328   approximately four weeks later. During this period the mean soil temperature of 13°C would not

329   have been limiting to N_2O production, however, low % soil WFPS would have been (Figures 1

330   and 2). A large rainfall event in early May (Figure 1) increased % soil WFPS from a mean value

331   of 27 % to 39 % which increased N_2O emissions (Figures 1 and 2). During the peaks in N_2O

332   emissions in August, % soil WFPS values were approximately 46 % (Figures 1 and 2), however,

333   at this time soil mineral N had returned to below what is considered a threshold level of 5 mg N

334   kg^{-1} (5.95 kg N ha^{-1}), which implies that soil WFPS has greater control over the potential for

335   N_2O production than soil mineral N contents. The relationship between flux response and % soil

336   WFPS was analysed for the highest N fertiliser treatment for this experiment. When N_2O data

337   from the one year measurement period is used, including periods in which soil NO_3^- is below 5

338   mg N kg^{-1}, there is a significant positive relationship between N_2O and soil WFPS ($p<0.001$)

339   (Figure 7a). When periods in which soil NO_3^- <5 mg N kg^{-1} are removed (Figure 7) there is also

340   a significant positive relationship between N_2O and soil WFPS ($p<0.001$) (Figure 7b), in

341   agreement with Dobbie et al. (1999) who also found a significant relationship ($p<0.05$) when the

342   same limitations were applied.

343   The observation of a significant relationship between N_2O emissions and % soil WFPS, even

344   when soil NO_3^- was < 5mg N kg^{-1} is in contrast to previous studies of Scottish arable sites which

345   found no relationship between these variables below an NO_3^- threshold of 5mg N kg^{-1} (Clayton

346   et al., 1997; Dobbie et al., 1999; Smith et al., 1998a). The relationship between N_2O flux and %

347   soil WFPS is related to the dominance of either nitrification or denitrification as the N_2O

348   producing processes. Davidson (1991) suggested that denitrification predominates at soil WFPS

349   >60 % and that at values <60 %, nitrification is the dominant process. In this study, despite

350   greater than average annual rainfall, the 60 % WFPS threshold was never exceeded. This

351 combined with the return of NH_4^+ concentrations to background levels prior to the NO_3^-

352 concentrations suggests that nitrification may have been the dominant N_2O production process.

353

354   *4.3 Emission intensities*

355 Crop yield increased with increasing rates of AN fertiliser application as expected due to the

356 greater availability of NO_3^- and NH_4^+ in the soil for uptake by the growing crop. However, it is

357 important to consider the amount of N_2O produced per unit of yield (yield scaled emissions, or

358 yield intensity). This allows assessment of a greater part of the treatment's "life cycle" than just

359 taking into account N_2O emissions, as ultimately for a fertiliser to be financially viable it must

360 produce sufficient crop yield. The recommended fertiliser application rate of 120 kg N ha^{-1},

361 which was used in this experiment had yield scaled emissions of 0.39 kg N_2O ton^{-1} grain. The

362 optimum fertiliser application rate would produce a high crop yield but minimal N_2O emissions,

363 and the results of this experiment demonstrate that the optimum fertiliser application would be

364 AN 160 kg N ha^{-1}. This application rate provided a higher crop yield than the 120 kg N ha^{-1}

365 application rate, but lower N_2O emissions, resulting in lower yield scaled emissions of 0.35 kg

366 N_2O ton^{-1} grain. Yield scaled emissions decreased with increasing rates of N fertiliser

367 application at low application rates from 1.15 kg N_2O ton^{-1} grain for the control treatment to 0.28

368 kg N_2O ton^{-1} grain for the AN 80 treatment. Although the yield scaled emissions from the AN 80

369 treatment are relatively similar to the yield scaled emissions from the optimum AN 160

370 treatment, it must be considered that crop yields from the AN 160 treatment are 40 % higher,

371 therefore it is advantageous to produce greater crop yields whilst not significantly increasing

372 yield scaled emissions. The yield scaled emission results obtained are in contrast to the results of

17

373   a meta analysis carried out by Van Groenigen et al. (2010), which reported the lowest emission

374   intensities following N application of 180-190 kg N ha^{-1}. We found no significant difference in

375   yield scaled emissions from applications of 40 -200 kg N ha^{-1} despite significantly greater crop

376   yields at N application rates of 160 and 200 kg N ha^{1}. Our yield scaled emission results indicate

377   that we must avoid under fertilising crops if we are to minimise the risk of enhancing N_2O

378   emissions whilst simultaneously obtaining poor crop yields.

379   *4.4 Mitigation option effects on N_2O emissions and crop yield*

380   The decrease in N_2O emissions through the use of the NI (DCD) is an important finding of this

381   research. The use of DCD has proven effective in reducing N_2O emissions in previous studies

382   conducted on grassland and spring barley sites in New Zealand and the UK (Di and Cameron,

383   2002, 2003; Di et al., 2007, 2010; McTaggart et al., 1997). However little work has been

384   undertaken to examine the effectiveness of DCD on arable soils in Scotland. A previous field

385   study in the UK investigating the effectiveness of DCD in reducing N_2O emissions from N

386   fertilised arable crops found a 36 % reduction in emissions from spring barley when DCD was

387   used (McTaggart et al., 1997). The successful inhibition of nitrification by DCD in this study is

388   evident due to the significantly increased levels of NH_4^+-N in the soils from the NI treatments

389   and decreased soil NO_3^--N contents, in combination with the decreased N_2O emissions. DCD

390   was more effective in reducing emissions from the AN 120 + NI treatment than from the urea

391   120 + NI treatment. This is in contrast to previous work which has demonstrated greater

392   decreases in N_2O emissions when DCD was applied to urea fertilised soils in comparison to AN

393   fertilised soils (McTaggart et al., 1997), as would be expected due to the higher quantities of soil

394   NH_4^+-N found in the urea treatment.

395   The potential of a 3 split AN fertiliser application and urea application (urea 120) to decrease

396   cumulative N_2O emissions in comparison to the AN 120 treatment was also apparent as

397   emissions were significantly decreased by 11 % and 26 % respectively. The decrease in N_2O

398   emissions associated with the use of a 3 split fertiliser application suggests that the nitrogen use

399   efficiency was increased. However, the mitigation effect was reasonably small and this might be

400   explained by the fertiliser application relatively early in the growing season. The lower N_2O

401   emissions from the urea 120 application in comparison to the AN 120 application is in agreement

402   with the findings of Dobbie and Smith (2003) and Smith et al. (2012). However, the results of

403   this study must be assessed with caution as ammonia (NH_3) emissions were not measured. Smith

404   et al. (2012) reported that 22 % of urea N applied to arable soil is emitted as NH_3, in comparison

405   to <3 % of ammonium nitrate N. The decrease in N_2O emissions associated with the urea

406   application in this study may therefore be a reflection of greater loss of NH_3 than from the AN

407   treatment resulting in lower soil mineral N concentrations and subsequently decreased potential

408   for N_2O emissions. Evidence for this can be seen in the soil NH_4^+ concentrations where the

409   initially high NH_4^+ concentration in the urea 120 treatment rapidly decreased to lower than the

410   levels seen in the AN 120 treatment, perhaps indicating volatilisation of NH_3. The decreased

411   N_2O emissions associated with the AN 120 (3 splits) and urea treatments were not associated

412   with increased crop yields as may be expected if greater retention of N within the soil was taking

413   place. Again, this supports the suggestion that considerable quantities of N could have been lost

414   in the form of NH_3 from the urea treatment.

415

416   A particularly interesting finding of this research is the significant decrease in crop yield

417   associated with the NI treatments. It was hypothesised that crop yield would be maintained or

418   increased during this experiment due to decreased rates of nitrification and reduced emissions of

419   N_2O and therefore maintenance of higher levels of NH_4^+ in the soil, providing greater N

420   availability for crop growth (Di and Cameron, 2002). However, it has been suggested that plants

421   may preferentially uptake NO_3^- from the soil due to greater ease of transport of NO_3^- through the

422   soil compared with NH_4^+ which is more tightly bound to the soil particles (Hofman and van

423   Cleemput, 2004). If the NI prevented conversion of NH_4^+ to NO_3^- by nitrification, then crop N

424   uptake and growth may suffer. The decrease in crop yield caused by the addition of a NI could

425   have implications for the adoption of NIs as an N_2O mitigation strategy by the farming

426   community, despite the financial benefits for the farmer associated with decreased loss of N

427   through N_2O emissions. The yield results observed in this experiment are in contrast to those

428   demonstrated in previous work in which DCD acted to increase crop or pasture yield (Di and

429   Cameron, 2002; Liu et al., 2013; Pain et al., 1994) or had no effect on crop yield (Weiske et al,

430   2001). The decrease in N_2O emissions combined with the decrease in crop yield observed from

431   the NI treatments resulted in a large (non significant) reduction in yield scaled emissions in

432   comparison to the non NI amended treatments by 31 % for the AN 120 + NI treatment and 40 %

433   for the urea 120 + NI treatment.

434   *4.5 Sampling period effects on N₂O emissions and emission factors*

435   This research demonstrated the considerable contribution of background emissions to emissions

436   recorded from applied treatments. Cumulative emissions from the control treatments represent 43

437   % of annual emissions from the highest N fertiliser treatment and 51 % of emissions from the

438   AN 120 treatment which are within the range of previously reported data. McTaggart et al.

439   (1997) reported background emissions that contributed 75 % of the emissions from spring

440   barley fertilised with 120 kg N ha^{-1}, and Smith et al. (2012) reported 26-67 % contribution of

20

441   control treatments to emissions from N fertilised treatments. This evidence suggests that

442   background emissions from unfertilised arable crops can be high and represents a considerable

443   proportion of the overall flux from fertilised crops. Smith et al. (2012) suggested that this high

444   background flux from arable sites is due to mineralisation of crop residues which is also likely to

445   have occurred at our experimental site following harvest of the previous oilseed rape crop.

446   Background emissions could also be considered as those occurring after the return of soil mineral

447   N to background levels, which in this experiment occurred during August 2011. Emissions after

448   this time could reflect crop residue inputs, N deep within the soil profile, remineralised fertiliser

449   N or treatment effects from previous fertiliser events, all of which may confound emissions from

450   the treatments of interest. Our work demonstrated the greatest cumulative monthly emissions in

451   August with mean cumulative N_2O-N emissions of 1.35 kg N_2O-N ha^{-1}. Previous research has

452   often not measured N_2O emissions for an entire year. For example, McTaggart et al. (1997)

453   measured emissions from sowing until early June and although Smith et al. (1998a) measured

454   N_2O emissions for a year from fertilisation, measurements were suspended during a period of

455   low fluxes in the summer and resumed again after autumn cultivation. If we had not taken

456   measurements during the summer, this period of high emissions would not have been recorded.

457   The large emissions during the summer months are suggested to be due to underlying natural

458   "background" variation in N_2O fluxes over space and time.

459   Although Bouwman (1996) and the IPCC recommend the use of N_2O emissions data from at

460   least 12 months of measurements in order to calculate EFs to achieve an accurate reflection of

461   management practices, we have calculated EFs over three timescales to analyse the effects of

462   background N_2O emissions on EFs. There were interesting variations between the seasonal and

463   annual EFs with annual EFs (-0.28 – 1.35 %) generally being greater than seasonal EFs (-0.04 –

464   0.86 %) (Table 2) due to the contribution of emissions over the winter period. Calculating EFs

465   over a longer time period did not always result in a greater EF, for example larger EFs were

466   commonly obtained over the 5 week calculation period in comparison to the seasonal period.

467   This is due to control emissions representing a lower proportion of total emissions immediately

468   following fertiliser application, and the subtraction of these from treatment emissions during the

469   EF calculation thereby causes greater calculated EFs. The question of which EF is more

470   appropriate to use depends on the desired outcome. Our findings indicate that, despite most

471   emissions usually occurring during the 5 week period after fertiliser application, the 5 week EF

472   calculation is inappropriate, when environmental conditions (e.g. rainfall and temperature) after

473   this time period are conducive to N_2O production. This work illustrated that there can be further

474   significant N_2O emissions which should be included in EF calculations to accurately reflect N_2O

475   EFs for arable soils. However, the decision to use a seasonal or annual EF is more complex. If it

476   is desirable to calculate an EF which accurately reflects the effects of specific treatments on N_2O

477   fluxes from arable soils then the results of this work suggest that a seasonal EF should be used in

478   order to remove the effects of background N_2O fluxes which are likely to be unrelated to the

479   applied treatments. Seasonal EFs may therefore provide a more accurate indication of the

480   emissions attributable to fertilisation and specific treatments which makes the use of year long

481   EFs for this purpose questionable. However, this would require removal of a large part of the

482   data set, which Smith et al. (2012) suggests would usually decrease the magnitude of calculated

483   EFs by 30 % in comparison to those which include a full year's data.

484   *4.6 Comparison to IPCC "default EF" and previously reported values*

485   The mean EFs calculated in this experiment are considerably lower than the IPCC's standard

486   EF1 value of 1.25 % which is currently applied to much of the UK, and also lower than the new

487   EF of 1 %. Mean annual and seasonal EFs were calculated for the purpose of comparison to the

488   IPCC standard value and as such only treatments within the normal range of fertilisation were

489   included (AN 80, AN 120, AN 160, Urea 120). In our study the mean annual EF from these

490   treatments was 0.79 % and the mean seasonal EF was 0.56 %. The EFs of the NI amended

491   treatments were lower than the mean annual EF, due to the decreased N_2O emissions associated

492   with these treatments, however the AN (3 splits) treatment EF was higher than the mean annual

493   EF although lower than the EF of the equivalent AN 120 treatment. The AN 120 treatment is

494   representative of the amount of N fertiliser which would be commercially applied in comparable

495   situations in Scotland. The annual EF for this treatment is 1.35 % which is greater than the IPCC

496   Tier 1 EF of 1.25 % or 1 %. Previous research into EFs from spring barley in Eastern Scotland

497   found EFs of 0.6 - 0.7 % (McTaggart et al., 1997; Smith et al., 1998 a,b), demonstrating a much

498   smaller range of EFs than those found in this experiment. It is suggested that the large range of

499   EFs obtained from this experiment are due to the range of fertiliser application rates, intense

500   sampling frequency and unexpectedly large emissions from the control plots. Also, the unusual

501   weather conditions over the study period which involved large amounts of rainfall over the

502   summer months during which time the treatment effects were no longer occurring, resulted in

503   large emissions which were not associated with individual treatments.

504   Smith et al. (1998a) compared EFs from Scottish arable and grassland sites to the data plotted by

505   Bouwman (1996) and found that N_2O emissions as a proportion of applied N, from the Scottish

506   sites, and in particular from the Scottish arable sites, are generally lower than from the rest of the

507   UK. This difference has been suggested to be due to lower temperatures in Scotland resulting in

508   lower N_2O emissions (Smith et al., 1998a). However, if just the EF calculated for the standard

509   fertiliser application rate (AN 120) is considered, then the EF is higher than the IPCC's 1.25 %

510   default EF and the new 1 % EF. Again, this is suggested to be due to the unusual weather

511   conditions experienced during the experimental period. Overall, the range of EFs obtained from

512   this experiment appear to support the movement from the IPCC's 1.25 % EF to the 1 % EF when

513   factors such as the climatic conditions are taken into account. It must also be considered that the

514   experiment was only one year in length, and that to obtain a more accurate view of EFs from

515   these treatments, more experiments of this type would be required in order to take into account

516   variables such as soil and climate.

517

518   **5. Conclusion**

519   This research demonstrated that area based emissions of N_2O are linearly related to N input,

520   supporting the IPCC's approach to calculating EFs. Soil % WFPS was shown to have a

521   significant effect on the magnitude of N_2O emissions and to have greater control over N_2O

522   production than soil mineral N. For this typical Scottish spring barley crop and soil system

523   receiving mineral fertiliser, the optimum fertiliser application rate is 160 kg N ha^{-1}, as indicated

524   by the calculated N_2O emission intensities of all treatments. Emission intensity results also

525   highlight the need to avoid under-fertilisation of crops if crop yields are to be maintained whilst

526   minimising N_2O emissions. The use of a NI, split fertiliser applications and urea instead of AN,

527   showed the potential to reduce N_2O emissions, however, the amendment of treatments with a NI

528   and 3 split treatment also decreased crop yield, raising questions over their suitability as N_2O

529   mitigation options in arable agriculture and prompting the need for further investigation. The

530   importance of the contribution of background emissions to calculated EFs was demonstrated and

531   the need for year long measurements of N_2O emissions is questioned. Calculated annual EFs

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532 were generally lower than the IPCC's default Tier 1 EF of 1.25 % and the new value of 1 %, but

533 largely support movement to, and use of, this new EF value, although further research in other

534 locations is required to assess its suitability for use throughout the UK.

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547 **References**

548 Abalos, D., Jeffery, S., Sanz-Cobena, A., Guardia, G. Vallejo, A. 2014. Meta-analysis of the

549 effect of urease and nitrification inhibitors on crop productivity and nitrogen use efficiency.

550 Agriculture Ecosystems & Environment 18, 136–144.

551

552

553   Amberger, A. 1989. Research on DCD as a nitrification inhibitor and future outlook.

554   Communications in Soil Science and Plant Analysis 20, 1933–1955.

555

556   Ball, B., Scott, A., Parker, J. 1999. Field N_2O, CO_2 and CH_4 fluxes in relation to tillage,

557   compaction and soil quality in Scotland. Soil and Tillage Research. 53, 29-39.

558

559   Bessou, C., Mary, B., Leonard, J., Roussel, M., Grehan, E., Gabrielle, B. 2010. Modelling soil

560   compaction impacts on nitrous oxide emissions in arable fields. European Journal of Soil

561   Science. 61, 348-363.

562

563   Bouwman, A. 1996. Direct emission of nitrous oxide from agricultural soils. Nutrient Cycling in

564   agroecosystems. 46, 53-70.

565

566   Burton, D., Zebarth, B., Gillam, K., MacLeod, J. 2008. Effect of split application of fertilizer

567   nitrogen on N2O emissions from potatoes. Canadian Journal of Soil Science. 88, 229-239.

568

569   Castellano, M., Schmidt, J., Kaye, J., Walker, C., Graham, C., Lin, H., Dell, C. 2010.

570   Hydrological and biogeochemical controls on the timing and magnitude of nitrous oxide flux

571   across an agricultural landscape. Global Change Biology. 16, 2711-2720.

572

573   Chadwick D., Cardenas L.M., Misselbrook T., Smith K.A., Rees R.M., Watson C., McGeough,

574   K.L., Williams J., Cloy J.M., Thorman R., Dhanoa D., 2014. Optimizing chamber methods for

575   measuring nitrous oxide emissions from plot-based agricultural European Journal of Soil Science

576   65 (2), 295-307.

577   Chapuis- Lardy, L., Wrage, N., Metay, A., Chotte, J., Bernoux, M. 2007. Soils, a sink for N_2O?

578   A Review. Global Change Biology. 13, 1-17.

579

580   Clayton, H., Arah, J., Smith, K. 1994. Measurement of nitrous oxide emissions from fertilized

581   grassland using closed chambers. Journal of Geophyiscal Research- Atmospheres. 99, 16599-

582   16607.

583

584   Clayton, H., McTaggart, I., Parker, J., Swan, L., Smith, K. 1997. Nitrous oxide emissions from

585   fertilised grassland: A 2-year study of the effects of N fertiliser form and environmental

586   conditions. Biology and fertility of soils. 25, 252-260.

587

588   Crutzen,P.J., Lelieveld, J. 2001. Human impacts on atmospheric chemisty. Annual Review of

589   Earth and Planetary Sciences. 29, 17-45.

590

591   Davidson, E. 1991. Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In

592   Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen

593   Oxides and Halomethanes, eds J. E. Rogers and W. B. Whitman, pp. 219-235. American Society

594   of Microbiology., Washington, District of Columbia.

595

596   Davidson,E.A. 2009. The contribution of manure and fertilizer nitrogen to atmospheric nitrous

597   oxide since 1860. Nature Geoscience. 2, 659-662.

598   De Kleine, C. and Harvey, M. 2012. Nitrous oxide chamber methodology guidelines. Global

599   Research Alliance.

600

601   Defra Fertiliser Manual 8th Edition (RB209). (2010) TSO: Norwich, pp 1-249

602   Di, H., Cameron, K., Sherlock, R. 2007. Comparison of the effectiveness of a nitrification

603   inhibitor, dicyandiamide, in reducing nitrous oxide emissions in four different soils under

604   different climatic and management conditions. Soil Use and Management. 23, 1–9.

605

606   Di, H., Cameron, K., Sherlock, R., Shen, J., He, J., Winfield, C. 2010. Nitrous oxide emissions

607   from grazed grassland as affected by a nitrification inhibitor, dicyandiamide, and relationships

608   with ammonia-oxidizing bacteria and archaea J Soils Sediments. 10, 943–954.

609

610   Di, H., Cameron, K. 2002. The use of a nitrification inhibitor, dicyandiamide (DCD), to decrease

611   nitrate leaching and nitrous oxide emissions in a simulated grazed and irrigated

612   Grassland. Soil Use and Management. 18, 395-403.

613

614   Di, H., Cameron, K. 2003. Mitigation of nitrous oxide emissions in spray irrigated

615   grazed grassland by treating the soil with dicyandiamide, a nitrification inhibitor. Soil Use and

616   Management. 19, 284-290.

617

618   Dobbie, K., McTaggart, I., Smith, K. 1999. Nitrous oxide emissions from intensive agricultural

619   systems: variations between crops and seasons, key driving variables, and mean emission factors.

620   Journal of Geophysical Research. 104, 26 981- 26 899

621

622   Dobbie, K., Smith, K. 2003. Nitrous oxide emission factors for agricultural soil in Great Britain:

623   the impact of soil water-filled pore space and other controlling variables. Global Change

624   Biology. 9, 204–218.

625

626   Farquharson, R., Baldock, J. 2008. Concepts in modelling N_2O emissions from land use. Plant

627   & Soil. 309, 147–167.

628

629   Flechard, C.R., Ambus, P., Skiba, U., Rees, R.M., Hensen, A., van Amstel, A., Pol-van

630   Dasselaar, A.V., Soussana, J.F., Jones, M., Clifton-Brown, J., Raschi, A., Horvath, L., Neftel, A.,

631   Jocher, M., Ammann, C., Leifeld, J., Fuhrer, J., Calanca, P., Thalman, E., Pilegaard, K., Di

632   Marco, C., Campbell, C., Nemitz, E., Hargreaves, K.J., Levy, P.E., Ball, B.C., Jones, S.K., van

633   de Bulk, W.C.M., Groot, T., Blom, M., Domingues, R., Kasper, G., Allard, V., Ceschia, E.,

634   Cellier, P., Laville, P., Henault, C., Bizouard, F., Abdalla, M., Williams, M., Baronti, S., Berretti,

635   F., Grosz, B. 2007. Effects of climate and management intensity on nitrous oxide emissions in

636   grassland systems across Europe. Agriculture Ecosystems & Environment. 121, 135-152.

637   Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean,

638   D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz., R. Van Dorland, 2007:

639   Changes in Atmospheric Constituents and in Radiative Forcing. In: Climate Change 2007: The

640   Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the

641   Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M.

642   Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press,

643   Cambridge, United Kingdom and New York, NY, USA.

29

644

645   GHG, 2013. www.ghgplatform.org.uk Last accessed 27th June 2013.

646

647   Hipkin, J. 1989. Humbie series. Soil map unit description. Soil Information For Scottish Soils

648   (SIFSS), The James Hutton Institute, UK.

649

650   Hoben, J., Gehl, R., Millar, N., Grace, P., Robertson, G. 2011. Nonlinear nitrous oxide (N_2O)

651   response to nitrogen fertilizer in on-farm corn crops of the US Midwest. Global Change Biology.

652   17, 1140–1152.

653

654   Hofman, G., van Cleemput, O. 2004. Soil and Plant Nitrogen. IFA, Paris, France.

655

656   Inselsbacher, E., Wanek, W., Ripka, R., Hackl, E., Sessitsch, A., Straussm S., Zechmeister-

657   Boltenstern, S. 2011. Greenhouse gas fluxes respond to different N fertilizer types due to altered

658   plant-soil-microbe interactions. Plant and Soil. 343, 17-35.

659

660   IPCC (Intergovernmental Panel on Climate Change), 1996. Revised 1996 IPCC Guidelines for

661   National Greenhouse Gas Inventories: Workbook, Module 4, Agriculture.

662

663   IPCC (Intergovernmental Panel on Climate Change), 2006. Chapter 11. N_2O emissons from

664   managed soils, and CO_2 emissions from lime and urea application. Volume 4. Agriculture,

665   Forestry and other land use. IPCC Guidelines for National Greenhouse Gas Inventories.

666

667   Jones, S., Rees, R.M., Skiba, U., Ball, B. 2007. Influence of organic and mineral N fertilizer on

668   N_2O fluxes from a temperate grassland. Agriculture, Ecosystems and Environment. 121, 74–83.

669

670   Lilly, A., Ball, B., McTaggart, I., Horne, P. 2003. Spatial and temporal scaling of nitrous oxide

671   emissions from the field to the regional scale in Scotland. Nutrient cycling in agroecosystems.

672   66, 241-257.

673

674   Liu, C., Wang, K., Zheng, X. 2013. Effects of nitrification inhibitors (DCD and DMPP) on

675   nitrous oxide emission, crop yield and nitrogen uptake in a wheat–maize cropping system.

676   Biogeosciences. 10, 2427–2437.

677

678   McSwiney, C., Robertson, G. 2005. Nonlinear response of N_2O flux to incremental fertilizer

679   addition in a continuous maize (*Zea mays* L.) cropping system. Global Change Biology. 11,

680   1712–1719.

681

682   McTaggart, I., Clayton, H., Parker, J., Swan, L., Smith, K. 1997. Nitrous oxide emissions from

683   grassland and spring barley, following N fertiliser application with and without nitrification

684   inhibitors. Biology and fertility of soils. 25, 261-268.

685

686   Pain, B., Misselbrook, T., Rees, Y. 1994. Effects of nitrification inhibitor and acid addition to

687   cattle slurry on nitrogen losses and herbage yields. Grass and Forage Science. 49, 209-215.

688

689   Pierzynski, G., Sims, S., Vance, G. 2005. Soils and Environmental Quality. 3rd Edition. Taylor

690   and Francis, Florida, USA.

691

692   Philibert, A., Loyce, C., Makowski, D. 2012. Quantifying Uncertainties in N2O Emission Due to

693   N Fertilizer Application in Cultivated Areas. PLoS ONE 7(11): e50950.

694   doi:10.1371/journal.pone.0050950.

695

696   Reay,D.S., Davidson,E.A., Smith,K.A., Smith,P., Melillo,J.M., Dentener,F., Crutzen,P.J. 2012.

697   Global agriculture and nitrous oxide emissions. Nature Clim.Change. 2, 410-416.

698

699   Rees, R.M., Baddeley, J., Bhogal, A., Ball, B., Chadwick, D., Macleod, M., Lilly, A., Pappa, V.,

700   Thorman, R., Watson, C., Williams, J. 2013. Nitrous oxide mitigation in UK agriculture. Soil

701   Science and Plant Nutrition. 59:1, 3-15.

702

703   Robertson, G. 1999. Standard Soil Methods For Long-Term Ecological Research. Edited by G.

704   Robertson [And Others]. Oxford University Press.

705

706   Saggar, S., Tate, K., Giltrap, D., Singh, J. 2008. Soil-atmosphere exchange of nitrous oxide and

707   methane in New Zealand terrestrial ecosystems and their mitigation options: a review. Plant and

708   soil. 309, 25-42.

709

710   Skiba, U., Ball, B. 2002. The effect of soil texture and soil drainage on emissions of nitric oxide

711   and nitrous oxide. Soil use and management. 18, 56-60.

712

713 Skiba, U., van Dijk, S., Ball, B. 2002. The infuence of tillage on NO and N_2O fluxes

714 under spring and winter barley. Soil use and management. 18, 340-345.

715

716 Smith, K., McTaggart, I., Dobbie, K., Conen, F. 1998a. Emissions of N_2O from Scottish

717 agricultural soils, as a function of fertilizer N. Nutrient cycling in agroecosystems. 52, 123-130.

718

719 Smith, K., Thomson, P., Clayton, H., McTaggart, I., Conen, F. 1998b. Effects of temperature,

720 water content and nitrogen fertilisation on emissions of nitrous oxide by soils. Atmospheric

721 environment 32:19, 3301-3309.

722 Smith, K., Ball, T., Conen, F., Dobbie, K., Massheder, J., Rey, A. 2003. Exchange of greenhouse

723 gases between soil and atmosphere: interactions of soil physical factors and biological processes.

724 European Journal of Soil Science. 54, 779-791.

725

726 Smith, K., Dobbie, K., Thorman, R., Watson, C., Chadwick, D., Yamulki, S., Ball, B. 2012. The

727 effect of N fertilizer forms on nitrous oxide emissions from UK arable land and grassland.

728 Nutrient cycling in agroecosystems. 93, 127-149.

729

730 Topp,C.F., Wang,W., Cloy,J.M., Rees,R.M., Hughes,G. 2013. Information Properties of

731 Boundary Line Models for N_2O Emissions from Agricultural Soils. Entropy. 15, 972-987.

732

733 Van Groenigen, J., Velthof, G., Oenema, O., Van Groenigen, K., Van Kessel, C. 2010. Towards

734 an agronomic assessment of N2O emissions: a case study for arable crops. European Journal of

735 Soil Science. 61, 903-913.

736

737 Wieske, A., Benckiser, G., Herbert, T., Ottow, J. 2001. Influence of the nitrification inhibitor

738 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous

739 oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated

740 application in field experiments. Biol Fertil Soils, 34:109–117.

741

742

743

744

745

746

747