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1 Isolating the effect of soil properties on agricultural soil greenhouse gas emissions under

2 controlled conditions

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6

7 Abstract

8 Agricultural soils are important sources of greenhouse gases (GHGs). Soil properties and 9 environmental factors have complex interactions which influence the dynamics of these GHG fluxes. 10 Four arable and five grassland soils which represent the range of soil textures and climatic conditions 11 of the main agricultural areas in the UK were incubated at two different moisture contents (50 or 80 % water holding capacity) and with or without inorganic fertiliser application (70 kg N ha⁻¹ ammonium 12 13 nitrate) over 22 days. Emissions of N₂O, CO₂ and CH₄ were measured twice per week by headspace 14 gas sampling and cumulative fluxes were calculated. Multiple regression modelling was carried out to 15 determine which factors (soil mineral N, organic carbon and total nitrogen contents, C:N ratios, clay 16 contents and pH) that best explained the variation in GHG fluxes. Clay, mineral N and soil C contents 17 were found to be the most important explanatory variables controlling GHG fluxes in this study. 18 However, none of the measured variables explained a significant amount of variation in CO₂ fluxes 19 from the arable soils. The results were generally consistent with previously published work. However, 20 N₂O emissions from the two Scottish soils were substantially more sensitive to inorganic N 21 fertilisation at 80% water holding capacity than the other soils, with the N_2O emissions being up to 22 107 times higher than the other studied soils. 23 Keywords: GHG emissions, inorganic fertiliser, agricultural soils 24 Running head: Agricultural soil greenhouse gas emissions

25 **1 Introduction**

Agricultural soils are important sources of atmospheric greenhouse gases (GHGs). Various soil properties, environmental factors and management practices have complex interactions which influence the dynamics of these GHG fluxes. Soil texture is a particularly important factor as it dictates soil water dynamics, pore space and gas diffusivity (Skiba & Ball 2002). The availability of nitrogen (N) for microbial processes is also an influential factor (Cardenas *et al.* 2019).

31 Greenhouse gas fluxes from agricultural soils are influenced by environmental factors such as 32 temperature, precipitation, and soil physical and chemical properties such as texture, pH, oxygen 33 concentration and nutrient availability. Texture affects pore space distribution and gas diffusivity 34 (Smith et al, 2003) whilst soil pH manipulates the microbial community structure, and therefore the 35 decomposition or accumulation of soil organic carbon (SOC) (Malik et al, 2018). The soil texture, 36 particularly the clay content, determines the level of physico-chemical stabilisation of SOC through 37 association with soil minerals (Schrumpf et al, 2013). Soil wetness strongly influences soil GHG 38 emissions. Production of N₂O by nitrification increases linearly as increasing soil water content 39 approaches 60% of water filled pore space (WFPS). At higher water contents denitrification becomes 40 more prevalent leading to maximum emissions at around 80% WFPS (Shepherd, 2009). Soil CO₂ 41 emissions decrease substantially after heavy rainfall because poor gas diffusivity and low air-filled 42 porosity restrict respiration and increase anaerobic conditions (Ball, 2013). Anaerobic soil conditions 43 can promote the production of CH_4 via methanogenesis whilst methanotrophy (CH_4 oxidation to CO_2) 44 is more prominent in aerated soils allowing diffusion of CH₄ into the soil from the atmosphere (Cloy 45 and Smith, 2015). In fine textured soils, pore spaces are smaller and so a lower volume of water is 46 required to reach the same WFPS as in a coarser textured soil. Limited diffusion in fine textured soils 47 therefore tends to support the development of anaerobic microsites and so tend to emit more N₂O than 48 coarser textured soils (Stehfest and Bouwmann, 2006).

49 Application of inorganic N such as ammonium nitrate (AN) fertiliser to soil temporarily creates an

50 excess of available-N required for microbial nitrification and denitrification (NH₄⁺ and NO₃⁻,

51 respectively) which reduces microbial competition for these resources (Norton and Firestone, 1996).

52 The application of inorganic N may also decrease or reverse the soil's CH₄ sink and source capacity
53 (Inselsbacher *et al*, 2011).

Across the UK, GHG emissions from agricultural soils vary widely as a consequence of climate, management and soil type. The objective of this study was to isolate the effect of soil chemical and physical properties on GHG emissions by measuring GHG fluxes from soils in a controlled environment. Soils were subjected to two different moisture contents with or without AN application.

58 2 Materials and Methods

59 2.1 Soils

60 Soils were collected from nine UK Agricultural Greenhouse Gas Research Platform sites: four arable

61 (Boxworth, Gilchriston, Rosemaund and Woburn) and five grassland (Crichton, Drayton,

62 Hillsborough, North Wyke and Pwllpeiran). The soils did not receive any N inputs from the end of the

63 2010 growing season to collection (February to early March 2011, McGeough *et al*, 2016). Soils were

64 sieved to < 4 mm to remove large stones and roots, air dried and stored in sealed plastic bags. These

65 sites represent the different soil types and climates of the main agricultural areas across the UK (Table

66 1).

67 2.2 Treatments

- 68 A fully-factorial experiment was designed with two water holding capacities (WHCs) (50% and
- 69 80%), and two AN application levels (0 or 70 kg N ha⁻¹). The method of Howard and Howard (1993)
- 70 and the following equation were used to determine WHC:

$$100\% \text{ WHC} = \frac{\text{mass saturated soil - mass oven dry soil}}{\text{mass oven dry soil}}$$

- 71 Treatments were applied in triplicate to 80 g of soil at a bulk density of ~1 g cm⁻³ (average value
- found from field measurements of these soils: range 0.6–1.6 g cm⁻³), in 500 ml Kilner jars.
- 73 Ammonium nitrate was dissolved in the deionised water used to adjust the WHC. Soils were

incubated at 10 °C (average annual temperature for all sites, Table 1) for 22 days, following a three
day pre-incubation period.

76 2.3 Headspace gas sampling

77 Headspace gas sampling was undertaken twice per week. Gas samples were taken from Kilner jars at 78 the beginning (t0) and end (t1) of a one hour closure period. Before each sampling period, jars were 79 opened for three minutes to allow gas concentrations in the jar to equilibrate with the laboratory air 80 before sealing the lids with both sampling ports open. The jars were flushed three times through one 81 sampling port using a 60 ml syringe before drawing a 30 ml t0 gas sample and injecting it into a 25 ml 82 pre-evacuated vial, after which both ports were closed. After the t0 headspace gas sampling, jars were 83 returned to the incubator and the 30 ml t1 samples were drawn one hour later with one port remaining 84 closed. Between sampling periods jar lids were closed with both ports open to allow free gas 85 exchange whilst limiting moisture loss. Moisture loss was never more than 1%, and so was not 86 deemed to be significant (calculated from mass change of kilner jars from beginning to end of 87 incubation).

88 2.4 GHG calculations

Gas samples were analysed for N₂O, CO₂ and CH₄ using an Agilent 7890A Gas Chromatograph (GC)
fitted with electron capture, flame ionisation and thermal conductivity detectors (Agilent
Technologies, Berkshire, UK) and a CTC Analytics COMBI PAL autosampler (CTC Analytics,
Hampshire, UK). The GC gas peak area responses were calibrated (calibration curves were linear for
CO₂ and CH₄, quadratic for N₂O) using four certified standard gas mixtures (BOC Industrial Gases,
UK). Headspace GHG concentrations were used to calculate GHG fluxes per day using linear
regression and the ideal gas law (Saggar *et al*, 2008):

96
$$F = \rho \frac{V}{A} \frac{\Delta C}{\Delta t} \frac{273.15}{T + 273.15}$$

97 This calculation assumes a linear increase in gas concentration in a known volume over a known 98 period of time, where F = flux, $\rho = gas$ density, V = jar volume, A = jar basal area, $\Delta c = difference$ between gas concentrations at t1 and t0, $\Delta t = jar$ closure time (hours), T = incubation temperature 100 (°C).

- 101 Cumulative fluxes were calculated using the trapezoidal rule (area under the curve) to interpolate
- 102 fluxes between sampling days (Hinton *et al*, 2015; Bell *et al* 2015a,b; Bell *et al*, 2016) as follows:
- 103 Cumulative flux = (day x cumulative flux + day y flux) + (mean (day x flux + day y flux))
- 104 * (day y day x 1)
- 105 Emission factors (EFs) define the percentage of applied N fertiliser which is emitted as N₂O.
- 106 Emission factors were calculated for N₂O emissions from AN fertilised soils incubated over the 22-
- 107 day incubation period using the following equation:

108
$$EF = \left(\frac{FN_2O \text{ flux } (kg N_2O - N) - CN_2O \text{ flux } (kg N_2O - N)}{N \text{ applied } (kg N)}\right) * 100$$

- where FN_2O = cumulative N₂O flux from fertilised soil and CN_2O = cumulative N₂O flux from unfertilised control soil.
- 111 Global warming potentials (GWPs) were calculated as CO₂ equivalents (CO₂-eq) using IPCC (2014)
- values over a 100-year timescale of 1, 28 and 265 for CO₂, CH₄ and N₂O respectively.

113 2.5 Chemical analyses

114 Pre- and post-incubation soil mineral N concentrations were determined. Soil subsamples were

115 extracted with 2 M KCl (1:2 soil to KCl) within 24 hours of the final headspace gas sampling.

- 116 Extracts were analysed for NH₄⁺-N and NO₃⁻-N using a Skalar San⁺⁺ continuous flow colorimetric
- autoanalyser (Skalar, York, UK). Colorimetric determination was carried out at wavelengths of 650
- 118 nm and 540 nm for NH_4^+ -N and NO_3^- -N, respectively, following the methods of Singh *et al* (2011).
- 119 Pre-incubation soil subsamples were extracted with deionised water (1:2) and soil solution pH was
- 120 measured using a calibrated pH electrode (Thermo-Orion, Beverly, MA, USA).

121 Air dried, ball milled soil samples were combusted and analysed for organic C (OC) and total nitrogen

122 (TN) using a Flash 2000 elemental analyser (Thermo Fisher Scientific, Bremen, Germany).

123 2.6 Statistical Analyses

124 Treatment effects (WHC and AN fertilisation) on cumulative GHG fluxes and pre- and post-

125 incubation mineral N contents were determined by two-way ANOVA. Significant differences

126 between EFs of different soils were determined by one-way ANOVA. Multiple linear regressions

127 were used to evaluate the influence of % clay (as a proxy for soil texture), % OC, % TN, C:N, pH and

128 NH₄⁺-N and NO₃⁻-N content on arable and grassland soils. Reduced models were determined by

129 backwards selection of the most significant variables. All statistics were carried out using Genstat

130 (15th edition). To more fully satisfy the assumption of normal distribution of the residuals data was log

transformed where appropriate and outlying cumulative GHG flux points were removed from the

analyses after scrutiny of the residuals.

133 3 Results

134 3.1 Soil properties

135 Ranges of soil properties across grassland soils were as follows: average TN content 0.27–0.77%;

average OC content 2.22–12.35%; average clay content 15.0–56.5%; C:N ratio 8.17–15.99 and pH

137 4.47–6.67. Ranges of soil properties across arable soils were as follows: average TN content 0.09–

138 0.19%; average OC content 0.94–1.90%; average clay content 11–45%; C:N ratio 8.21–13.57 and pH

139 5.13–7.91. Specific values for each soil are given in Table 1. Average clay contents were taken from

140 McGeough et al (2016). These differences in soil properties are due to natural variation in geology,

141 topography and climate.

142 3.2 GHG fluxes

143 Global warming potentials (CO₂-eq) for grassland and arable soils (Table 2) show that the GHG

144 budgets were generally dominated by N_2O and CO_2 fluxes.

145 $3.2.1 N_2O$ emissions

146 The Scottish arable and grassland 80% WHC+N treatment soils had substantially higher N₂O

emissions than the other soils (p < 0.05, Figure 1a,b). The Scottish grassland soil 80% WHC treatment

148 was also significantly higher than other treatments in all soils except one (Pwllpeiran) (p < 0.05,

149 Figure 1b).

150 During the 22-day incubation period N₂O EFs calculated for the arable and grassland soils (Figures

151 2a, b) were consistently below the IPCC default value of 1%. This was expected since EFs are usually

152 calculated from one year field measurements however, the EFs calculated here are useful for site

153 comparisons. At 50% WHC the EFs were negligible. The Scottish soils had significantly higher EFs

154 (p < 0.01) than the other soils at 80% WHC.

155 The negative EFs observed for Boxworth and Crichton 50% WHC do not indicate uptake of N₂O

156 from the atmosphere, but rather that the emissions from the unfertilised control treatments were

157 greater than from the fertilised treatments. There were no significant differences between emissions

158 from fertilised and unfertilised soils in these cases where negative EFs were observed.

159 3.2.2 CO₂ fluxes

160 There was high variability in cumulative CO₂ fluxes between replicates in the grassland and arable

soils. For instance, CO₂ fluxes from Crichton soils at 50% WHC were $2760 \pm 1450 \text{ mg CO}_2\text{-C m}^{-2}$,

162 Hillsborough soils at 50% WHC+N had fluxes of $945 \pm 532 \text{ mg CO}_2$ -C m⁻², at 80% WHC Drayton

soil had fluxes of $8890 \pm 2350 \text{ CO}_2\text{-C} \text{ m}^2$ and the 80% WHC+N North Wyke soils had fluxes of 382

164 \pm 3400 CO₂-C m⁻² (Figure 3a). Measured apparent negative or zero CO₂ fluxes are considered to be

165 due to analytical constraints near the detection limit of the GC.

166 3.2.3 CH₄ fluxes

167 The CH₄ fluxes calculated for each sampling day provided evidence that both methanogenesis and

168 methanotrophy were occurring simultaneously in all soils with some alternating strongly between

being a source and a sink (Figure 4a,b). Calculated cumulative fluxes can be assumed to reflect the

dominant process in each soil and treatment combination. Cumulative CH₄ fluxes were highly
variable within arable soils (Figure 4a).

172 3.3 Mineral N concentrations

173 For all soils there were large differences between initial untreated pre-incubation soil NO₃⁻N

174 contents, but not corresponding NH₄⁺-N contents (Figure 5). Unfertilised and AN fertilised

175 post-incubation Hillsborough and North Wyke grassland soils exhibited greatest loss or microbial

transformation of native soil NO₃⁻-N and added fertiliser NO₃⁻-N. Results for the unfertilised post-

177 incubation Crichton grassland soils suggest net production of NH₄⁺-N via OM mineralisation.

178 Fertilisation with AN had a significant effect on NO₃⁻-N and NH₄⁺-N contents for both grassland and

arable soils (p < 0.001) with increases of 5 (50% WHC) and 25 (80% WHC) times relative to

180 unfertilised soils being observed.

181 3.4 Bivariate Correlations

Pre-incubation NO₃⁻-N contents were positively correlated with OC, TN and pre-incubation NH₄⁺-N contents and negatively correlated with soil ph. Soil TN and pH were positively correlated with clay content and C:N ratio was negatively correlated with clay content (Table 3). Soil C:N ratio was correlated positively with pH and C:N, OC and TN contents were all positively correlated to each other.

187 3.5 General Linear Modelling

188 Results from both full and reduced models are shown for arable (Table 4) and grassland (Table 5)

soils. For all models, except for the arable cumulative CO_2 flux, the full model explained 1–2% more

190 of the variation than the reduced model. For arable cumulative N₂O fluxes, the reduced model

explained 60% of the variation with significant positive correlations with OC (p < 0.01) and NO₃⁻-N

- 192 (p < 0.05) contents, and negative correlation with clay contents (p < 0.01). For grassland cumulative
- 193 N₂O fluxes the reduced model explained 69% of the variation with significant negative correlations

with NO₃⁻-N (p < 0.01) and clay (p < 0.01) contents and positive correlation with NH₄⁺-N (p < 0.01) contents.

196 The negative correlation between N_2O flux and clay content seems to be atypical and is caused by the 197 high emissions and low clay contents of the two Scottish soils (Gilchriston and Crichton). When these 198 two soils were removed from the analysis the relationship became positive.

It was not possible to adequately describe the variation of cumulative CO_2 fluxes from the arable soils with the measured variables. CO_2 fluxes from arable soils were much more variable from day to day than from grassland soils. The full model described only 2% of the variation. The reduced models explained 52% of the variation for cumulative CO_2 fluxes from the grassland soils. Cumulative CO_2 fluxes had significant (p < 0.01) positive correlations with NH_4^+ -N and clay contents and significant negative correlation with NO_3 -N contents.

The reduced model for arable cumulative CH₄ fluxes explained 37% of the variation with significantly positive correlations with TN contents (p < 0.01) and % WHC (p < 0.05), and negative correlation with clay contents (p < 0.001). The reduced model for grassland cumulative CH₄ fluxes explained 18% of the variation with a significant positive correlation with OC contents (p < 0.01).

209 4 Discussion

210 4.1 N₂O fluxes and emission factors

211 In this study, all soils were processed and incubated in the same way but the two Scottish soils 212 displayed substantially higher N_2O fluxes than the other soils, particularly at the higher moisture 213 content. However, laboratory and field studies investigating the soils from these sites have reported 214 varying results. McGeough et al (2016) found much higher N₂O emissions from the Scottish grassland soil studied here (60% WFPS, incubated at 15 °C for 60 days, 100 μ g N g⁻¹ dry soil), 215 216 although not from the Scottish arable soil. In field trials, Bell et al (2015b) found that the annual EF 217 for the Scottish arable soil was ~3 to 5 times higher than grassland sites elsewhere in the UK. 218 However, Cardenas et al (2019) did not observe higher annual EFs from the Scottish grassland site in field measurements when compared to other UK grassland sites across a range of N application rates
(80 - 400 kg N ha⁻¹).

In these controlled incubations, clay, mineral N and OC contents were found to be the most important
factors in determining N₂O fluxes from arable and grassland soils. Clay content (and therefore
texture) has frequently been identified as an important factor controlling soil N₂O emissions (Skiba
and Ball, 2002; Dobbie and Smith, 2003; Stehfest and Bouwmann, 2006). Positive correlations
between N₂O flux and OC content have also previously been observed (Stehfest and Bouwmann,
2006).

In this study, EFs were consistently below the value assumed in the IPCC Tier 1 methodology (1%)

228 (IPCC, 2006a). It should be noted that the 22 day incubation period used in this study was much

shorter than the 12 months normally used to assess EFs, however, it does provide a valuable ranking

230 of the proportion of emissions that can be attributed to the added N source.

231 Field experiments at the Scottish sites have also reported low EFs in the short term after AN

application. Hinton et al (2015) found EFs from 0.44–0.56% for the five weeks following AN

application, but annual EFs of 1.36, 0.96 and 1.08% for AN application rates of 120, 160 and 200 kg

N ha⁻¹ at the Scottish arable site. Smith *et al* (2012) found an EF of 0.61% (over the growing season)

at the Scottish grassland site in 2004, however, the EF in 2003 was higher (1.13%). EFs are highly

variable, values between 0.2 and 7% have been reported for agricultural fields in Scotland (Clayton et

al, 1997; Smith *et al*, 1998; Dobbie *et al*, 1999) and the range of uncertainty associated with the IPCC

238 default value is 0.3–3.0% (IPCC, 2006b).

It has been suggested that the higher EFs from Scottish sites is due to the incidence and intensity of rainfall (and therefore WFPS) at the time of fertiliser application (Dobbie *et al*, 1999). However, this does not explain the higher EFs from Scottish soils under controlled conditions. Soil OC stocks are higher in Scottish agricultural soils (compared with elsewhere in the UK) (Bradley *et al*, 2005) and so

the distribution and availability of soil OC pools may differ. Further investigation of OC pools and

their availability, aggregate-stabilising minerals and microbial communities within the UK soils
studied here may explain these unexpected findings.

246 4.2 CO₂ fluxes from UK arable and grassland agricultural soils

A positive correlation between grassland CO_2 fluxes and clay content was found in this study, which is counter to the theory that higher clay contents provide a greater opportunity for chemical protection

of OM by adsorption. Dilustro *et al* (2005) also observed greater CO₂ fluxes from clay textured

250 (> 19% clay) than sandy textured (< 12% clay) forest soils. However, they attribute this to a more

dense vegetation (and so greater root respiration) on the clay soils and the sandy soils being

excessively drained for part of the study period.

In this study, grassland soil CO_2 flux showed a positive correlation with NH_4^+ -N content and a

negative correlation with NO_3^-N content. However, fertilisation with AN was observed to decrease or have no effect on CO_2 emissions. Zaman *et al* (2002) speculate that fertilisation without the addition

256 of C cannot drive increased microbial growth or respiration. There are several conflicting results in

the literature which show increases (Baggs *et al*, 2003), decreases (al-Kaisi *et al*, 2008) and no effect
(Baggs *et al*, 2003; Garcia-Ruiz and Baggs, 2007 and al-Kaisi *et al*, 2008) of AN fertilisation on CO₂
flux.

260 4.3 CH₄ fluxes from UK arable and grassland agricultural soils

Individual soils showed highly variable CH_4 fluxes throughout the incubation period, the oscillation of fluxes from net source to net sink indicates that methanogenesis and methanotrophy were occurring simultaneously (Ekberg and Christensen, 2006). As a result the net emissions of CH_4 when expressed as CO_{2e} was small relative to the other greenhouse gases. Soil moisture content, native N content and clay content explained significant variation in emissions from arable soils and OC content from grassland soils.

267 Soils with coarse textures have higher oxidation rates of CH₄ than more fine textured soils,

attributable to low porosity and high water retention in fine textured soils causing low gas diffusivity

269 into the soil (Dörr *et al*, 1993; Dutaur and Verchot, 2007; Tate *et al*, 2007).

In this study increasing the moisture content from 50 to 80% WHC actually reduced emissions (increased sinks) in all cases except one. It is possible that the methanotrophic microbial population was under water stress at the lower WHC level. von Fischer *et al* (2009) found that methanotrophic activity dropped off sharply below 40% WFPS in a sandy loam grassland soil. The presence of NO_3^- N would also act as an inhibitor to methanotrophs as this would be used in preference to organic carbon as a terminal electron acceptor.

276 4.4 Overall GHG budget

277 When expressing the GHG fluxes measured from incubated soils in this study in terms of their GWPs, 278 it is clear that the GHG budget is driven by N_2O and CO_2 fluxes. However, under field conditions 279 much of the CO_2 released from soil by respiratoin is returned by photosynthesis and so may not be a 280 net source of atmospheric CO_2 . This highlights the importance of accurately assessing the effects of 281 agricultural soil management on N_2O emissions (Gao *et al.* 2018).

282 Conclusions

283 Generally, the results were in support of those found in the literature for a wide range of soils, 284 conditions and locations with soil texture, soil mineral N and OC contents found to be the most 285 important measured variables controlling GHG fluxes. However, the N2O emissions from Scottish soils were more sensitive to ammonium nitrate fertilisation, particularly at 80% WHC, than the other 286 287 UK agricultural soils studied here. The reason for the high EFs from Scottish soils remains unclear, 288 however, it is possible that it could be linked to differences in the structure of the microbial 289 population or composition of the soil organic matter pools. Resolving this issue would be valuable in 290 making more precise predictions of N₂O emissions in response to soil management.

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295 **References**

- al-Kaisi, M.M., Kruse, M.L. and Sawyer, J.E. (2008) Effect of nitrogen fertilizer application on
- 297 growing season soil carbon dioxide emission in a corn-soybean rotation. Journal of Environmental
- 298 *Quality* 37:325–332
- 299 Baggs, E.M., Stevenson, M.P., Pihlatie, M., Regar, A., Cook, H. and Cadisch, G. (2003) Nitrous oxide
- 300 emissions following emissions following application of residues and fertiliser under zero and
- 301 conventional tillage. *Plant and Soil* 254:361–370
- 302 Ball, B.C. (2013) Soil structure and greenhouse gas emissions: a synthesis of 20 years of
- 303 experimentation. European Journal of Soil Science 64:357–373
- 304 Bell, M.J., Rees, R.M., Cloy, J.M., Topp, C.F.E., Bagnall, A. and Chadwick, D.R. (2015a) Nitrous
- 305 oxide emissions from cattle excreta applied to a Scottish grassland: Effects of soil and climatic
- 306 conditions and a nitrification inhibitor. Science of the Total Environment 508:343-353
- 307 Bell, M.J., Hinton, N., Cloy, J.M., Topp, C.F.E., Rees, R.M., Cardenas, L., Scott, T., Webster, C.,
- 308 Ashton, R.W., Whitmore, A.P., Williams, J.R., Balshaw, H., Paine, F., Goulding, K.W.T. and
- 309 Chadwick, D.R. (2015b) Nitrous oxide emissions from fertilised UK arable soils: Fluxes, emission
- 310 factors and mitigation. *Agriculture, Ecosystems & Environment* 212, 134-147.
- 311 Bell M.J., Cloy J.M., Topp C.F.E., Ball B.C., Bagnall A., Rees R.M., Chadwick D.R., (2016)
- 312 Quantifying N₂O emissions from intensive grassland production: the role of synthetic fertiliser type,
- 313 application rate, timing, and nitrification inhibitors, Journal of Agricultural Science
- 314 doi.org/10.1017/S0021859615000945
- 315 Bradley, R.I., Milne, R., Bell, J., Lilly, A., Jordan, C. and Higgins, A. (2005) A soil carbon and land
- 316 use database for the United Kingdom. Soil Use and Management 21:363-369
- 317 Cardenas, L.M., Bhogal, A., Chadwick, D.R., McGeough, K., Misselbrook, T., Rees, R.M., Thorman,
- 318 R.E., Watson, C.J., Williams, J.R., Smith, K.A. & Calvet, S (2019) Nitrogen use efficiency and
- 319 nitrous oxide emissions from five UK fertilised grasslands. Science of the Total Environment
- 320 661:696-710

- 321 Clayton, H., McTaggart, I.P., Parker, J., Swan, L. and Smith, K.A. (1997) Nitrous oxide emissions
- 322 from fertilised grassland: a 2-year study of the effects of N fertiliser form and environmental
- 323 conditions. *Biology and Fertility of Soils* 25:252–260
- 324 Cloy, J.M. and Smith, K.A. (2015) Greenhouse Gas Emissions. In: Reference Module in Earth
- 325 Systems and Environmental Sciences Online reference database, Elsevier, Oxford.
- 326 Dilustro, J.J., Collins, B., Duncan, L. and Crawford, C. (2005) Moisture and soil texture effects on
- soil CO2 efflux components in soiutheastern mixed pine forests. *Forest Ecology and Management* 204:85–95
- 329 Dobbie, K.E., McTaggart, I.P. and Smith, K.A. (1999) Nitrous oxide emissions from intensive
- 330 agricultural systems: Variation between crops and seasons, key driving variables, and mean emission
- 331 factors. Journal of Geophysical Research 104:26891–26899
- 332 Dobbie, K.E. and Smith, K.A. (2003) Nitrous oxide emission factors for agricultural soils in Great
- Britain: the impact of soil water-filled pore space and other controlling factors. *Global Change Biology* 9:204–218
- 87
- Dörr, H., Katruff, L. and Levin, I. (1993) Soil texture parameterization of the methane uptake in
 aerated soils. *Chemosphere* 26:697–713
- 337 Dutaur, L. and Verchot, L.V. (2007) A global inventory of the soil CH₄ sink. *Global Biogeochemistry*
- 338 *Cycles* 21 doi: 10.1029/2006GB002734
- 339 Ekberg, A. and Christensen, T.R. (2006) Wetlands and methane emission. In Encyclopaedia of Soil
- 340 Science, Second Edition. Ed. Lal, R. New York, USA.
- Gao, B., Huang, T., Ju, X., Gu, B., Huang, W., Xu, L., Rees, R.M., Powlson, D.S., Smith, P. & Cui, S. 2018.
- 342 Chinese cropping systems are a net source of greenhouse gases despite soil carbon sequestration.
- 343 *Global Change Biology*, **24**, 5590-5606.

- 344 Garcia-Ruiz, R. and Baggs, E.M. (2007) N₂O emission from soil following combined application of
- 345 fertiliser-N and ground weed residues. *Plant Soil* 299:263–274
- Hinton, N.J., Cloy, J.M., Bell, M.J., Chadwick, D.R., Topp, C.F.E. and Rees, R.M. (2015) Managing
- 347 fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated
- 348 Cambisol in Scotland. Geoderma Regional 4:55–65
- Howard, D.M. and Howard, P.J.A. (1993) Relationships between CO₂ evolution, moisture content and
- temperature for a range of soil types. Soil Biology and Biochemistry 25:1537–1546
- 351 Inselsbacher, E., Wanek, W., Ripka, K., Hackl, E., Sessitsch, A., Strauss, J. and Zechmeister-
- 352 Boltenstern, S. (2011) Greenhouse gas fluxes respond to different N fertilizer types due to altered
- 353 plant-soil-microbe interactions. *Plant Soil* 343:17–35
- 354 IPCC (Intergovernmental Panel on Climate Change) (2006a) 2006 IPCC Guidelines for national
- 355 greenhouse gas inventories. IGES, Japan
- 356 IPCC (Intergovernmental Panel on Climate Change) (2006b) N₂O emissions from managed soils, and
- 357 CO₂ emissions from lime and urea application. Chapter 11. Agriculture, Forestry and other land use.
- 358 vol. 4. IPCC Guidelines for National Greenhouse Gas Inventories
- 359 IPCC (Intergovernmental Panel on Climate Change) (2014) Climate Change 2014: Synthesis Report.
- 360 Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental
- 361 Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva,
- 362 Switzerland
- 363 Malik, A.A., Puissant, J., Buckeridge, K.M., Goodall, T., Jehmlich, N., Chowdhury, S., Soon Gweon,
- H., Peyton, J.M., Mason, K.E., van Agtmaal, M., Blaud, A., Clark, I.M., Whitaker, J., Pywell, R.F.,
- 365 Ostle, N., Gleixner, G. and Griffiths, R.I. (2018) Land use driven change in soil pH affects microbial
- 366 carbon cycling processes. *Nature Communications* 9:3591

- 367 McGeough, K.L., Watson, C.J., Müller, C., Laughlin, R.J. and Chadwick, D.R. (2016) Evidence that
- 368 the efficacy of the nitrification inhibitor dicyandiamide (DCD) is affected by soil properties in UK
- 369 soils. Soil Biology and Biochemistry 94:222-232
- 370 Norton, J.M. and Firestone, M.K. (1996) N dynamics in the rhizosphere of *Pinus Ponderosa*
- 371 seedlings. Soil Biology & Biochemistry 28:351–362
- 372 Saggar, S., Tate, K.R., Giltrap, D.L. and Singh, J. (2008) Soil-atmosphere exchange of nitrous oxide
- and methane in New Zealand terrestrial ecosystems and their mitigation options: a review. *Plant Soil*309:25–42
- 375 Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I. and Schulze, E.D. (2013)
- 376 Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and
- 377 attachment to minerals. *Biogeosciences* 10:1675–1691
- 378 Shepherd, T.G. (2009) Visual Soil Assessment. Volume 1. Field guide for pastoral grazing and
- 379 cropping on flat rolling country. 2nd Edition, Horizons Regional Council, Palmerston North, New
- 380 Zealand, pp. 119.
- 381 Singh, U., Sanabria, J., Auston, E.R. and Agyin-Birikorang, S. (2011) Nitrogen transformation,
- ammonia volatilization loss, and nitrate leaching in organically enhanced nitrogen fertilizers relative
- 383 to urea. Soil Science Society of America Journal 76:1842–1854
- Skiba, U. and Ball, B. (2002) The effect of soil texture and soil drainage on emissions of nitric oxide
 and nitrous oxide. *Soil Use and Management* 18:56–60
- 386 Smith, K.A., McTaggart, I.P., Dobbie, K.E. and Conen, F. (1998) Emissions of N₂O from Scottish
- agricultural soils, as a function of fertilizer N. Nutrient Cycling in Agroecosystems 52:123–130
- 388 Smith K.A., Ball, T., Conen, F., Dobbie, K.E., Massheder, J. and Rey, A. (2003) Exchange of
- 389 greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological
- 390 processes. European Journal of Soil Science 54:79–791

- 391 Smith, K.A., Dobbie, K.E. Thorman, R., Watson, C.J., Chadwick, D.R., Yamulki, S. and Ball, B.C.
- 392 (2012) The effect of N fertilizer forms on nitrous oxide emissions from UK arable land and grassland.
- 393 Nutrient Cycling and Agroecosystems 93:127–149
- 394 Stehfest, E. and Bouwman, L. (2006) N₂O and NO emission from agricultural fields and soils under
- 395 natural vegetation: summarizing available measurement data and modelling of global annual
- 396 emissions. Nutrient Cycling in Agroecosystems 74:207–228
- Tate, K.R., Ross, D.J., Saggar, S., Hedley, C.B., Dando, J., Singh, B.K. and Lambie, S.M. (2007)
- 398 Methane uptake in soils from *Pinus radiate* plantations, a reverting shrubland and adjacent pastures:
- 399 Effects of land-use change, and soil texture, water and mineral nitrogen. Soil Biology & Biochemistry
- 400 39:1437–1449
- 401 Von Fischer, J.C., Butters, G., Duchateau, P.C., Thelwell, R.J. and Siller, R. (2009) In situ measures
- 402 of methanotroph activity in upland soils: A reaction-diffusion model and field observation of water
- 403 stress. Journal of Geophysical Research 114: doi: 10.1029/2008JG000731
- 404 Zaman, M., Cameron, K.C., Di, H.J. and Inubushi, K. (2002) Changes in mineral N, microbial
- 405 biomass and enzyme activities in different soil depths after surface applications of dairy shed effluent
- 406 and chemical fertilizer. *Nutrient Cycling in Agroecosystems* 63:275–290

Land Use	Site	Average annual temp. (°C)	Soil texture	Annual rainfall (mm)	100% WHC (g water g ⁻¹ soil)	TN (g N kg ⁻¹ soil)	OC (g C kg ⁻¹ soil)	C:N ratio	Clay (% by weight)	рН
Grassland	Crichton	10.2	Sandy Ioam	> 950	0.55 (0.03)	3.06 (0.163)	32.6 (1.52)	10.68 (0.046)	12.5	5.3 (0.03)
	Drayton	10.3	Clay	0 - 750	0.51 (0.04)	4.62 (1.383)	50.8 (15.60)	11.01 (0.477)	50.1	6.6 (0.42)
	Hillsborough	9.8	Clay Ioam	751 - 950	0.34 (0.04)	7.72 (0.107)	12.4 (0.77)	15.99 (0.077)	28.1	5.9 (0.03)
	North Wyke	9.6	Silty clay	> 950	0.64 (0.03)	2.72 (0.060)	22.2 (0.83)	8.17 (0.089)	32.5	4.5 (0.02)
	Pwllpeiran	9.3	Clay Ioam	> 950	0.70 (0.16)	4.41 (0.638)	41.8 (6.06)	9.49 (0.035)	23.8	5.1 (0.10)
Arable	Gilchriston	8.7	Sandy Clay Ioam	< 750	0.45 (0.02)	0.93 (0.023)	12.7 (0.53)	13.57 (0.213)	12.7	5.9 (0.03)
	Woburn	10.9	Loamy sand	< 750	0.45 (0.04)	0.86 (0.037)	9.4 (0.40)	10.93 (0.027)	10	7.0 (0.08)
	Rosemaund	10.4	Clay Ioam	751 - 950	0.30 (0.05)	1.28 (0.062)	10.5 (0.18)	8.21 (0.163)	20.9	5.1 (0.02)
	Boxworth	9.7	Clay	550	0.51 (0.00)	1.85 (0.043)	19.0 (0.35)	10.27 (0.036)	44.8	7.9 (0.05)

Table 2

Treatment	Land Use	Site	N ₂ O	CO ₂	CH ₄
50%	Arable	Boxworth	651	1460	10.97
WHC		Gilchriston	477	985	4.07
		Rosemaund	-41.0	301	12.25
		Woburn	21.1	-90.6	5.95
	Grassland	Crichton	884	2760	-0.82
		Drayton	298	2040	-33.28
		Hillsborough	-61.4	140	33.34
		North Wyke	128	1060	-0.41
		Pwllpeiran	99.9	-168	-6.69
50%	Arable	Boxworth	394	2090	20.32
WHC+N		Gilchriston	570	1740	4.58
		Rosemaund	-49.1	2770	32.18
		Woburn	-2.8	1840	0.35
	Grassland	Crichton	495	2750	-21.1
		Drayton	331	3720	10.38
		Hillsborough	-8.4	945	21.87
		North Wyke	169	1990	-4.07
		Pwllpeiran	-13.9	-263	17.29
80%	Arable	Boxworth	463	1130	6.56
WHC		Gilchriston	1450	1440	-7.1
		Rosemaund	-81.8	1980	5.28
		Woburn	75.3	363	-26.06
	Grassland	Crichton	1300	4780	-19.66
		Drayton	411	8890	-8.64
		Hillsborough	109	2550	26.71
		North Wyke	297	3390	-1.35
		Pwllpeiran	41.6	437	-21.29
80%	Arable	Boxworth	1436	1560	21.48
WHC+N		Gilchriston	12300	1220	-6.43
		Rosemaund	-56.9	891	38.04
		Woburn	114	-69.9	-20.11
	Grassland	Crichton	182000	1780	-20.12
		Drayton	1840	6390	1.54
		Hillsborough	127	3810	12.57
		North Wyke	1230	382	-13.4
		•			
		Pwllpeiran	74.5	938	-2.71

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	Clay	OC	TN				
	(% by	(% by	(% by			NH4 ⁺ -N	NO₃⁻-N
Variate	weight)	weight)	weight)	C:N ratio	рН	(mg kg⁻¹)	(mg kg ⁻¹)
clay	1.00						
OC	0.19	1.00					
TN	0.33 *	0.96 *	1.00				
C:N	-0.21 *	0.69 *	0.51 *	1.00			
pН	0.26 *	-0.06	-0.16	0.27 *	1.00		
NH4+-N	0.00	0.02	0.01	0.01	0.02	1.00	
NO₃ ⁻ -N	0.09	0.27 *	0.31 *	0.00	-0.23 *	0.89 *	1.00

Table 4

	Arable CO ₂				Arable N ₂ O				Arable CH ₄				
	Full Model		Reduced Mo	odel	Full Model		Reduced Mode		Full Model		Reduced Mode		
Variable	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE	
NO ₃ N content	-1732	4.33			0.00048	0.000671	0.0003 ****	0.0000					
NH4+-N content	-2.43	4.36			-0.000178	0.000684			-0.0003	0.0002			
% WHC	19	15.4			0.0061	0.0032			0.0146 ****	0.0065	0.0146 ****	0.0066	
OC content	3024	2535	1082	604	2.798 *	0.486	2.723 *	0.328					
TN content	-19479	23840							94.4 **	28.2	72.9 *	18.5	
C:N ratio									0.0851	0.0827			
Clay content					-0.0658 *	0.013	-0.0638 *	0.0089	-0.243 **	0.078	-0.1855 *	0.0535	
рН													
Constant	-1732	1458	-392	818	-2.361 *	0.454	-1.774	0.259	-7.73 **	2.56	-5.59 *	1.2	
F	p = 0.328		p = 0.08		*		*		*		*		
R ²	0.02		0.05		0.61		0.60		0.39		0.37		

Table 5

Variable	Grassland (CO ₂			Grassland N ₂		Grassland CH₄					
	Full Model		Reduced Model		Full Model		Reduced Model		Full Model		Reduced Model	
	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE
NO ₃ N content	7.32	8.73	-6.26 *	1.24	-0.0022 **	0.0007	-0.0018 *	0.0002	0.0030	0.0035		
NH4+-N content	-4.46	8.86	9.32 *	1.41	0.0028 *	0.0007	0.0023 *	0.0002	-0.0033	0.0035		
% WHC	8.8	17.1			0.003	0.0024			0.0120	0.0067		
OC content					-0.094	0.114			0.008	0.437	0.1036 *	0.0279
TN content	-39464	24582			2.26	3			-8.08	8.96		
C:N ratio	2108	1239							0.549	0.608		
Clay content	113.9 *	33.6	88.7 *	19.5	-0.00537	0.00427	-0.008 **	0.0028				
рН	2127	1458			-0.206	0.206			0.253	0.564		
Constant	-22114	12672	526	818	1.466	0.608	0.7506*	0.0806	-5.36	5.99	-0.509 **	0.184
F	*		*		*		*		***		*	
R ²	0.54		0.52		0.70		0.69		0.20		0.18	

Table 1: Land use, average annual temperature (°C), soil texture, annual average precipitation for the nine soils, **p**re-incubation average 100% water holding capacity (WHC), total nitrogen (N) and, organic carbon (OC) contents, C:N ratios, clay contents and pH for the grassland and arable agricultural soils.

Table 2: Global warming potentials (CO₂-eq) of grassland and arable soils incubated over a 22 day period at 50 or 80% water holding capacity (WHC) and with or without ammonium nitrate (N) fertiliser.

Table 3: Bivariate correlations between measured soil properties (pre-treatment) for all nine soils. Clay, organic carbon (OC), total nitrogen (TN) NH_4^+ -N and NO_3^- -N contents, pH and C:N ratio. * Significant correlations (p < 0.05).

Table 4: Full and reduced multiple linear regression models for arable soils. Variables assessed were NO_3 -N and NH_4^+ -N contents (mg kg⁻¹), % water holding capacity (WHC), organic carbon (OC) and total nitrogen contents (TN) (% by weight), C:N ratios, clay content (% by weight) and pH. CV is the coefficient of variance, SE is the standard error. Significance levels are denoted as follows: * p < 0.001, ** p < 0.005, *** p < 0.01, **** p < 0.05.

Table 5: Full and reduced multiple linear regression models for grassland soils. Variables assessed were NO₃⁻⁻N and NH₄⁺-N contents (mg kg⁻¹), % water holding capacity (WHC), organic carbon (OC) and total nitrogen (TN) contents (% by weight), C:N ratios, clay content (% by weight) and pH. CV is the coefficient of variance, SE is the standard error. Significance levels are denoted as follows: * p < 0.001, ** p < 0.005, *** p < 0.01, **** p < 0.05.

Figure 1: Cumulative N₂O fluxes (mg N₂O-N m⁻²) from a) arable and b) grassland soils for 50% water holding capacity (WHC) (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) treatments over a 22 day incubation period. Two-way ANOVA. * p < 0.001, ** p < 0.005, *** p < 0.05.

Figure 2: Emission factors (%) for N₂O emissions from ammonium nitrate fertilised soils (70 kg N ha^{-1}): a) arable soils at 50% and 80% WHC (water holding capacity), b) grassland soils at 50% and 80% WHC. B = Boxworth, G = Gilchriston, R = Rosemaund, W = Woburn, C = Crichton, D = Drayton, Hillsborough = H, N = North Wyke, P = Pwllpeiran.

Figure 3: Cumulative CO₂ fluxes (mg CO₂-C m⁻²) for a) arable and b) grassland soils for 50% water holding capacity (WHC) (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) treatments over a 22 day incubation period. Measured apparent negative or zero CO₂ fluxes are considered to be due to analytical constraints near the detection limit of the GC.

Figure 4: Cumulative CH₄ fluxes (mg CH₄-C m⁻²) for a) arable and b) grassland soils for 50% water holding capacity (WHC) (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) treatments over a 22 day incubation period.

Figure 5: a) Arable soil NO₃⁻-N, b) grassland soil NO₃⁻-N, c) arable soil NH₄⁺-N and d) grassland soil NH₄⁺-N contents for untreated pre-incubation (Pre-inc) soils and 50% WHC (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) post-incubation soils. Bars with different letters are significantly different. B = Boxworth, G = Gilchriston, R = Rosemaund, W = Woburn, C = Crichton, D = Drayton, Hillsborough = H, N = North Wyke, P = Pwllpeiran.



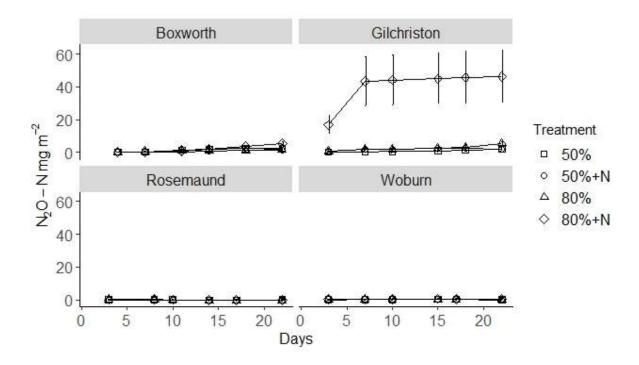
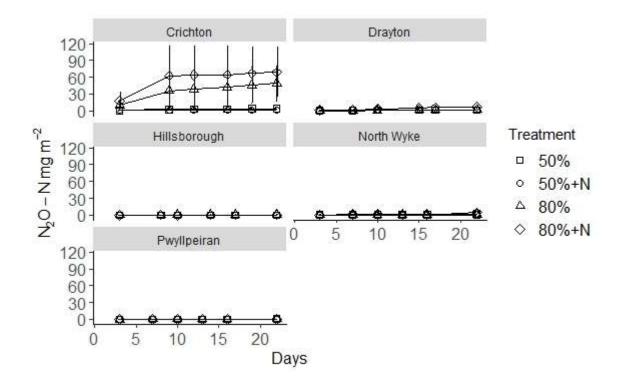
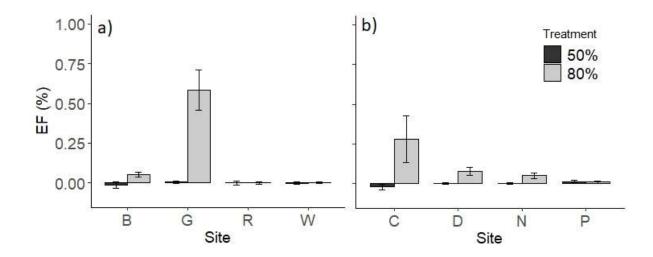


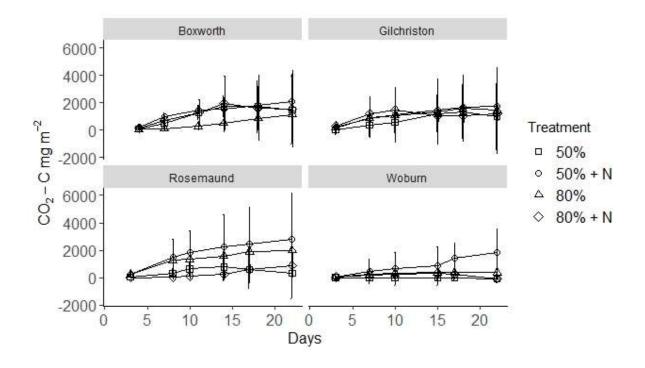
Figure 1b)













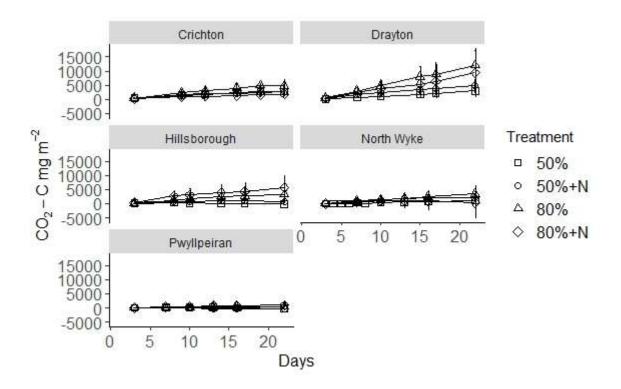


Figure 4a)

