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1	Optimizing farmyard manure and cattle slurry applications for intensively
2	managed grasslands based on UK-DNDC model simulations
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13 Abstract

14 Fertilizer applications can enhance soil fertility, pasture growth and thereby increaseing 15 production. Nitrogen fertilizer has, however, been identified as a significant source of nitrous 16 oxide (N₂O) emissions from agriculture if not used correctly and can thereby increase the 17 environmental damage costs associated with agricultural production. The optimum use of organic fertilizers requires an improved understanding of nutrient cycles and their controls. Against this 18 context, the objective of this research was to evaluate the scope for reducing N₂O emissions from 19 20 grassland using a number of manure management practices including more frequent applications 21 of smaller doses and different methods of application. We used a modified UK-DNDC model and 22 N₂O emissions from grasslands at Pwllpeiran (PW), UK, during the calibration period in autumn, 23 were 1.35 kg N/ha/y (cattle slurry) and 0.95 kg N/ha/y (farmyard manure), and while 2.31 kg 24 N/ha/y (cattle slurry) and 1.08 kg N/ha/y (farmyard manure) during the validation period in spring, 25 compared to 1.43 kg N/ha/y (cattle slurry) and 0.29 kg N/ha/y (farmyard manure) during the spring 26 at North Wyke (NW), UK. The modelling results suggested that the time period between fertilizer 27 application and sample measurement (TPFA), rainfall and the daily average air temperature are 28 key factors for N₂O emissions. Also, the emission factor (EF) varies spatio-temporally (0-2%)compared to the assumed uniform 1% EF used by theassumption of IPCC. Predicted N₂O 29 30 emissions were positively and linearly ($R^2 \approx 1$) related with N loadings under all scenarios. During 31 the scenario analysis, the use of high frequency, low dose fertilizer applications compared to a 32 single one off application was predicted to reduce N_2O peak fluxes and overall emissions for cattle 33 slurry during the autumn and spring seasons at the PW and NW experimental sites by 17% and 34 15%, respectively. These results demonstrated that an optimised application regime using outputs 35 from the modelling approach is a promising tool for supporting environmentally-friendly precision agriculture. 36

37 Keywords

38 UK-DNDC, emission factor, farmyard manure, greenhouse gases (GHG), nitrous oxide, cattle39 slurry

40

41 **1. Introduction**

42 Grazed grasslands provide us with food, biodiversity, and landscapes of high aesthetic quality,
43 whilst also offering considerable potential to enhance carbon storage and watershed functioning

(Xu et al., 2019; Chianese et al., 2009). Grasslands and intensively managed pasture represent 44 45 about 30% of the total global land use area and about 70% of the total agricultural expanse (Latham 46 et al., 2014). Grazing livestock produce 33%–50% of global total agricultural gross domestic 47 product (GDP) (Herrero et al., 2013). However, a number of challenges and risks exist for grazing 48 ecosystems due to a range of interconnected factors including, climate change, excessive nutrient 49 runoff, soil degradation, water shortages, changes in market demands, nitrous oxide (N_2O) 50 emissions and over-grazing (Pulido et al., 2018; Thomas et al., 2018; Orr et al., 2016; Chen et al., 51 2008; Baral et al., 2014; Kim et al., 2014).

52 Agricultural soils contribute about 65% of global nitrous oxide (N_2O) emissions (Reay et al., 2012), and this greenhouse gas has a warming potential of approximately 300 times that of carbon 53 54 dioxide (CO₂) over 100 years. In the UK, agriculture contributes up to 75% of N_2O emissions, of 55 which 75% originate from agricultural soils following nitrogen fertilizer (both synthetic and 56 organic) applications (Brown et al., 2016). In addition to the greenhouse effect, N_2O also plays an 57 important role in ozone depletion (Smith, 2017). It has been reported that the contributions of organic fertilizer applications to N₂O emissions in the EU were approximately equal to 85% of 58 synthetic fertilizers (Velthof et al., 2015). 59

Key components of grassland management include grazing intensity resulting from livestock stocking density and grazing regime, fertilization applications and, in some environmental settings, irrigation. Fertilizer inputs are important for pasture and forage productivity and corresponding livestock productivity (Bump and Baanante, 1996). However, fertilizer nitrogen can be a significant source of N₂O emissions from agriculture if not used correctly (Bodirsky et al., 2012). Furthermore, fertilizer use is very expensive in terms of both private and public costs. Optimized livestock production can reduce negative environmental impacts and assist adaptation to climate 67 change if site-specific best management practices (BMP) are targeted to the four critical areas of 68 on-farm nutrient management (source, rate, time and place) (Patil et al., 2018; Goulding et al., 69 2008). As a result, much effort has been made to assess the influence of inorganic and organic fertilizers on nutrient cycles, N₂O emissions and soil health (Bhogal et al., 2011; Evanylo et al., 70 2008; Patil et al., 2018; ,Li et al., 2013; Noirot- Cosson et al., 2017; Diego et al., 2017). For 71 72 example, Pires et al., (2015) reported that the currently excessive use of N fertilizers not only 73 decreases efficiency, but also increases the CO_2 concentrations in atmosphere. The optimum use 74 of inputs using the 4R (Right source, Right rate, Right time, and Right place) principles will 75 enhance the efficiency, reduce the emissions, and improve the economic conditions of those persons directly and indirectly attached with the farming sector. Lassaletta et al., (2014) concluded 76 that more than half of the total N applied to the vegetation without following the 4R technique 77 78 hasis no beneficial impactuse and subsequently degrades affects the sustainability of land, air, and 79 water resources over theon a longer terms. Patil et al., (2018) showed that effective scheduling of 80 organic fertilizers improves the quantity and quality of sunflowers compared to recommended traditional practices. 81

Organic fertilizer applications have potential benefits for grassland compared to synthetic 82 83 fertilizers, including: (1) increasing soil organic matter; (2) improving soil quality; (3) producing 84 organic foods, and; (4) increasing productivity (Zheng et al., 2010; Wang, 2014; FAO, 2017). 85 Consequently, organic fertilizers, such as FYM and cattle slurry (CS), are increasingly applied in 86 agriculture because of these wide-ranging benefits. However, organic fertilizers are more complex 87 than synthetic fertilizers due to varying compositions, as evidenced, for example, by the substantial 88 range in C/N ratios from 13 for FYM to 2 for cattle slurry (Bouwman et al., 1997; McTaggart et 89 al., 1999; Akiyama et al., 2004; Green, 2015). Factors such as compositional variability mean that

90 it is more challenging to optimize organic fertilization management in grasslands in terms of91 timing, frequency, and rates of application.

92 Process-based models, such as Denitrification and Decomposition (DNDC), can simulate the dynamics of nutrient cycles, soil carbon, and greenhouse gas (GHG) emissions for assisting the 93 improved understanding of nitrogen cycles and their controls in grassland systems. DNDC can, 94 95 for instance, help reduce the need for replicated laboratory and fileld experiments and optimize 96 organic fertilizer management (Shen et al., 2018a; 2018b; Li et al., 1992; Yadav and Wang, 2017). 97 Gilhespy et al., (2014) presented the different phases of DNDC development for taking into 98 account integrated affects of soil, climate, vegetation type, management practices, and biogeochemical processes. Zhang and Niu (2016) reviewed the plant growth sub-model of DNDC. 99 100 Shen et al. (2018a) modified the UK-DNDC model to analyse the effects of green compost and 101 FYM applied on winter wheat and grasslands on N₂O fluxes at three UK research farms, whilst 102 Shen et al., (2018b) studied N_2O emissions associated with slurry and digestate applications. The 103 latter study reported that although organic fertilizers enhance soil fertility and crop yields, they 104 have the potential tobut might increase N₂O emissions due to lower carbon and nitrogen ratios. While Shen et al. (2018a; 2018b) developed DNDC functions for new organic fertilizers, such as 105 106 digestate and green compost, the effects of fertilization management and seasonality were not 107 simulated at the study sites. Many studies have shown, nevertheless, that N_2O emissions can be 108 affected significantly by fertilization management including type (inorganic, organic), application 109 timing, application rate, method of application (Deng et al., 2016; Zhao et al., 2016), and 110 environmental factors including seasonality. Therefore, there is a need for combining newly 111 available field data and modelling tools, such as DNDC, to explore optimized organic fertilization

112 management under site-specific combinations of climate, soil and grazing, as captured by existing113 UK research farms.

Because DNDC can be used for a Tier 3 approach to estimating the emission factors (EF) for N₂O, it has been widely used for simulations of annual N₂O emissions from various agricultural soils treated with CS and FYM, including accounting for spatial and temporal variabilities (Kim et al., 2013; Shen et al., 2018a,b). DNDC requires a range of input data including, for example, soil hydraulic, chemical property, vegetation, and climatic parameters. The simplified regression model for N₂O emission factors can therefore be a useful means of simplifying the data needs of process-based tools.

121 In this study, the overall aim was to evaluate the efficiency and impacts of fertilizer management, 122 (i.e. manure application rate and split applications in grassland systems), on N_2O emissions. The 123 research hypothesis was: split fertilizer applications according to crop physiological stages, as 124 opposed to a one time application, can optimize farm management for reducing N₂O emissions. 125 The specific objectives were: (1) to assess the effects of fertilizer management, in the form of 126 more frequent doses and different application methods, on N₂O emissions in grasslands; (2) to 127 simulate N₂O fluxes from two UK soils treated with FYM and CS fertilizers using the UK-DNDC 128 model parameterised for specific soil, time between fertilizer application and measurement, and 129 environmental factors, (3) to determine emission factors based on simulated N_2O emissions due 130 to application of the two fertilizers to soils, and; (4) to develop a meta-model to explore the effects 131 of climatic parameters (average daily temperature, precipitations) and the time interval (days) 132 between fertilizer application and subsequent (different times) sample measurements (TPFA) on 133 N₂O emissions.

134 **2. Material and Methods**

135 **2.1. Research Sites**

136 Two UK research sites were selected at Pwllpeiran (PW), Wales, and North Wyke (NW), England 137 (Fig. 1) for sensitivity analysis of DNDC under different environment and management conditions. These two farms provide suitable datasets for two years (2011-2012) for representing variability 138 139 in soil and climatic conditions (Nicholson et al., 2017; Cardenas et al., 2010; 2019; Orr et al., 140 2016). Table 1 summarisesshows the research site coordinates, soil physical and chemical 141 properties, climatic data, manure application scheduling data, and crop type for different 142 treatments during the autumn and spring at PW, and spring at NW. The treatments comprised a 143 control, plus FYM and CS inputs using surface broadcasting (CS-SB), and CS application using a 144 trailing shoe (CS-TS).

145

146 <Figure 1>

147

148 <Table 1> 149

The FYM is generated by beef cattle dung, urine, bedding material (such as straw) and uneaten forage, whereas the CS comprises dung, urine and includes rainwater if stored in an uncovered store (Pain and Menzi, 2011). The plants have immediate access to the small portion of N available in organic amendments; however, the remaining larger percentage of N is available after the decomposition of FYM. Irrigation water was not applied Dduring the experimental periods at the two research farms., irrigation water was not applied.

156 **2.2. The DNDC model**

157 2.2.1. Model description

Li et al. (1992) developed the process-based DNDC model for simulation of GHG emissions (EPA,

159 1995) in the USA. DNDC is composed of ecological drivers (climate, soil, vegetation, and human

160 activity) and soil environmental factors (temperature, moisture, pH, E_h, and substrates NH₄⁺, NO₃⁻, 161 DOC after decomposition). The soil temperature and moisture profiles are determined by the soil 162 and climate module. Depending on the soil and climatic conditions, the vegetation module of 163 DNDC numerically simulates daily crop growth, nitrogen uptake, and root respiration. As a result, 164 this module calculates biomass yields. The crop growth module is again composed of sub-routines 165 for controlling management practices such as crop rotation, tilling, irrigation, fertilizer 166 applications, and manure additions (Li et al., 1994). The decomposition module consists of four 167 soil carbon pools forincluding litter, microbial biomass, humads, and humus. This module 168 simulates daily substrates (NH_4^+ , NO_3^- , DOC) as a function of prevailing soil temperature and 169 moisture.

The final module for nitrification and denitrification has we been improved using the concept of the anaerobic balloon, which swells and shrinks as a function of soil redox potential (Li et al., 2004). The substrates (such as DOC, NH_4^+ and NO_3^-) allocated to the anaerobic or aerobic compartments of each layer enable nitrification and denitrification processes to occur simultaneously.

For the current study, we used UK-DNDC because this version has been calibrated and validated 175 176 under the UK-specific conditions for soil and climate combinations. In UK-DNDC, the soil is 177 considered as a series of discrete horizontal layers ranging from 0-50 cm depth. Some soil 178 properties (bulk density, porosity, hydraulic parameters) are assumed to be constant in each layer, 179 but most of the soil properties (soil moisture, temperature, pH, field capacity, wilting point, carbon and nitrogen pools) can vary between layers. The model simulates dynamic variables for each 180 181 layer for each time step. Since the observed data collected at the two study sites was measured at 182 10 cm soil depth, the model simulations were used to output predictions at the same depth.

183 **2.2.2. Input parameters**

Input parameters are daily weather data, soil physical and chemical properties, plants, and agricultural practices. Agricultural practices include tillage, fertilization, manuring, irrigation, and grazing/cutting. The soil parameters, including soil pH, SOC, NO₃⁻, NH₄⁺ for both study sites, are summarised in Table 1. The total N (kg-N/ha) contents in organic fertilizers for the CS-SB, CS-TS, and FYM treatments applied during <u>the</u> autumn and spring at PW and <u>the</u> spring at NW are also shown in Table 1.

Table 2 presents the nitrogen loadings for two fertilizers applied at the study sites, following the methods of Kim et al., (2013). The default C/N ratios were considered in DNDC to determine the carbon loading of FYM and CS treatments applied to the two study sites (Table 2). The term factor used in Table 2 shows the nitrogen loading according to Kim et al. (2013) for the reference case (factor = 1), 1.5 times the reference, and 2 times the reference.

195 Measurements of direct N₂O-N were made using 5 static chambers (0.8 m² total surface area) per 196 plot over 12 months after manure applications. Gas samples were analysed by gas chromatography. 197 The measured daily fluxes were regressed through linear gas accumulation. For further details, 198 readers are referred to Chadwick et al. (2014) and Nicholson et al. (2017). Standard protocols were 199 deployed for measuring soil moisture and soil temperature (Nicholson et al., 2017; Cardenas et al., 2010; Orr et al., 2016).

201 <Table 2>

For comparing and controlling the N_2O peak and overall annual emissions, CS was applied by two different methods, including one single time application and split applications according to the grass crop physiological stages (Moore et al., 1991) as shown in Table 3.

205 <Table 3>

As the soil at the two experimental sites is typically wet given the prevailing climatic conditions on the western side of the UK, UK-DNDC simulations assumed field capacity initially, with soil moisture varying from that point onwards as a function of soil and climatic parameter variability during the simulation period.

210 **2.3. Emission factors for nitrous oxide**

The emission factor (EF) is a measure of transformation proficiency of nitrogen available in fertilizer into N₂O emissions:

213
$$\text{EF} = \frac{N_2 O_f - N_2 O_c}{N_a} 100\%$$
 (1)

Where: N_2O_f is the total N₂O produced from the fertilized soils (kg N/ha/y); N_2O_c is the N₂O produced from the soil without application of fertilizer (kg N/ha/y), and; N_a is the total nitrogen (kg N/ha/y) available in the fertilizer applied to the soil.

The default EF fixed by IPCC Tier 1 is 0.01 (1%) and is related with N_2O emissions due to fertilizer applications to in agricultural soils (Eggleston et al., 2006). The net emission flux, N_{net} , is strongly linear with N_{a} :

$$220 \quad N_{net} = EF \times N_a \tag{2}$$

221 2.4. Statistical measures for UK-DNDC performance evaluation

The performance of UK-DNDC was evaluated using the observed N_2O emission data at the two UK sites. <u>The Ccoefficient of determination (R²) and the root mean square error (RMSE) wereare</u> used for <u>testing model performance</u> index of how well the modeled results reproduce observed data. The relative error (RE) <u>wasis</u> used to compare approximations between the modeled results and the observed data:

227
$$R^{2} = \frac{\left(\sum_{i=1}^{n} (S_{i} - S_{m,i})(O_{i} - O_{m,i})\right)^{2}}{\sum_{i=1}^{n} (S_{i} - S_{m,i})^{2} (O_{i} - O_{m,i})^{2}}$$
(3)

228 RMSE =
$$\sqrt{\frac{\sum_{i=1}^{n} (S_i - O_i)^2}{n}}$$
 (4)

$$RE = \frac{O_i - S_i}{O_i}$$
(5)

Where: the subscripts *i* and *m* represent the index number and average value, respectively. The symbols *S* and *O* are UK-DNDC simulated and observed values, respectively. *n* is the total number of values. Based on the research objectives, statistical criteria for evaluating model performance were set as $R^2>0.5$, and average RMSE<0.5.

234 **2.5. UK-DNDC** calibration and validation

The UK-DNDC simulations were performed from 1 January to 31 December (Julian days) and annual (365 days) simulated and observed values were used to compare the cumulative N₂O emissions. The UK-DNDC model calibration was based on autumn and validation for spring at PW. The trapezoidal rule of interpolation <u>wasis</u> used to calculate the observed annual fluxes between measurement points.

240 The UK-DNDC model was tested against the datasets of water filled pore space (WFPS), soil 241 temperature and N₂O emissions from the two study farms (Fig. 1). We firstly calibrated and 242 validated the WFPS and soil temperature to calculate their correlation coefficient, R^2 , (Eq. 3), 243 RSME (Eq. 4) and RE (Eq. (5). (Fig. 2). Then, we calibrated and validated daily N₂O flux (Figs. 3, 244 4 and 5). We also calibrated annual N₂O emissions (Figs., 6 and 7). The best fitness parameters 245 were obtained by finding the maximum coefficient of determination (R^2) and the minimum root 246 mean square error, RMSE (%), through OFAT (one factor at a time) analysis. After calibration, 247 the RMSE between annual observed and simulated values for N₂O emissions reduced from 2.7 248 (3.48 kg N/ha/y) to 1.51 (2.31 kg N/ha/y) in the case of the CS-SB treatment, and from 2.31 (3.49 249 kg N/ha/y) to 1.19 (2.33 kg N/ha/y) for CS-TS in the spring at PW. After calibrationed and 250 validationed, UK-DNDC was used to simulate different rates of nitrogen loading to explore relationships between nitrogen loading and annual N_2O emissions under site-specific conditions and to explore optimal organic fertilizer applications and strategies in the two intensively managed grassland settings.

254 **2.6.** Nitrous oxide flux and <u>a</u>EF linear model

As there is <u>a</u> strong relationship between N_2O flux and N loading applied to agricultural soils, a linear regression model can be developed for reducing the input and calculation requirements (Cardenas et al., 2010).

258
$$w = aN + b$$
 (6)

259
$$a = \frac{w(N) - w(control)}{N} = EF$$
(7)

Where: *w* and *N* represent the N₂O emission flux (kg N/ha/y) and nitrogen loading (kg N/ha/y), respectively. The slope "*a*" is equivalent to <u>the</u> EF and intercept "*b*" is the controlled emission flux (kg N/ha/y).

Although equation (6) is fit to describe the linear relationship on an annual basis, this relationship does not work on a daily time step due to the spatio-temporal variability of soil properties and climate change impacts (Laville et al., 2011).

266 **3. Results and discussion**

We examined the performance of UK-DNDC against the observed data for WFPS, soil temperature, and N_2O emissions at the two study sites. We subsequently performed scenario analyses to explore optimal timing, and applications for organic fertilizers.

270 **3.1. Daily WFPS and soil temperature**

The UK-DNDC model simulates soil temperature based on WFPS (%) and soil hydraulic properties at a daily time step. Although the averaged observed event rainfall at both PW and NW

is in the range of 7-10 mm, the variability of rainfall is different in terms of variance and standard

274 deviation. This variability has an important influence on N₂O emissions. The simulated and 275 observed WFPS (%) for both locations are in good agreement in terms of relative error (RE: 0.09-276 0.15) and RMSE (0.11-0.17), but the magnitude of the R^2 (0.12-0.27) is low (Fig. 2A). The reason 277 for this relates to the irregular time intervals of the observed values. In the UK-DNDC model, the 278 simulated values of WFPS are continuous and based on the previous time step value (Shen et al., 279 2018a). The model fit could be further improved by collecting continuous observed values, but 280 this option is physically impossible. Fig.2B shows that the model captured the variations in soil 281 temperature and matched the observed data well. However, the air temperature is slightly lower 282 than the soil temperature due to being open to the atmosphere in both locations and climates. This 283 can be explained by the fact that the UK-DNDC model simulates soil temperature and WFPS (%) 284 using the thermos-hydraulic model at a daily time step. Because the heat transfer in soil is 285 calculated using the Fourier law, the soil temperature is a balance between heat dissipation and 286 soil heat capacity. When the heat capacity is larger than heat dissipation, the soil temperature could 287 be slightly higher than the air temperature due to being open to the atmosphere in both locations and climates. Also, the continuous aerobic and anaerobic chemical reactions and subsequent heat 288 289 transfer between soil layers is slow so more heat is kept in the soil, resulting in a warmerhotter 290 internal soil layer than the atmosphere.

291 *<*Figure 2A>

292 <Figure 2B>

293 **3.2. Daily nitrous oxide fluxes**

Fig. 3A shows the observed and simulated values for N_2O emissions for the four treatments including CS surface broadcasting (CS-SB, Fig. 3A(c)), CS trailing shoe (CS-TS, Fig. 3A(d)), and FYM (Fig. 3A(b)), plus the and control treatment (Fig. 3A(a) for the autumn at PW. The simulated 297 values of N₂O emissions follow the same trend of the observed values, but again the model fit is 298 poor due to the irregular interval of the observed measurements. ForIn the control and FYM 299 treatments (Fig. 3A(a), 3A(b)), the magnitude of N2O emissions varied between 0-12 g-N/ha/d, 300 but the treatments (Fig. 3A(c), 3A(d)) showed higher emission ranges between 0-80 g-N/ha/d. This 301 greater magnitude is due to CS applications of 24 kg-N/ha in both treatments compared to the 302 control. The FYM treatment received 131 kg-N/ha but the emission was in the same range as the 303 control treatment, reflecting the fact that readily available nitrogen is only 0.9 kg/ha in FYM 304 compared to 9.4 kg/ha for the CS treatments. For daily N₂O fluxes, CS holds more water than 305 FYM. UK-DNDC generally over-predicts N₂O emissions. This could be due to poor representation 306 of water factors in the denitrification process, in which the water is assumed to be constant. The N 307 loading rates were low compared to typical applications. In the latter, the application rates normally 308 vary between 200-250 kg N/ha for FYM and 150-400 kg-N/ha in the case of CS (Thomas and Hao, 309 2017; Kim et al., 2013). The lower application rates at the study sites reduced the N₂O emissions. 310 The decision of whether to apply FYM or CS depends on the soil fertility status, crop N demand, 311 and level of precision technology available for supporting field application. At the experimental 312 sites, the soil fertility is relatively good and N demands are limited due to the prevalence of short 313 root grassland compared with longer root crops; therefore, the application rates of CS and FYM 314 are quite low compared to typical application rates reported more generally. At the experimental 315 sites, the gradient <u>of</u> application rates wasere used for a comparison <u>of among</u> lower and higher 316 rates.

317 <Figure 3A>

Fig. 3B compares the observed and simulated values of N₂O emissions for the three treatments
(CS-SB, CS-TS, and FYM) and control-treatment for the spring at PW. The simulated values for

320 N₂O emissions follow the same trend of the observed values, but again the model fit was not good 321 because of the irregular interval of observed measurements (TPFA). In the control and FYM 322 treatment (Fig. 3B(a), 3B(b)), the magnitude of N₂O emissions varied between 0-20 g-N/ha/d, 323 compared with the higher magnitude of between 0-130 g N/ha/d for the treatments (Fig. 3B(c), 324 3B(d)). This greater magnitude reflected the CS applications of 67 kg N/ha in both treatments. In 325 contrast, the FYM treatment received a nitrogen application of 122 kg N/ha but the emissions were 326 in the same range as the control-treatment, reflecting the fact that readily available nitrogen in 327 FYM is only 0.5 kg/ha compared to 35 kg/ha for the CS treatments. Here, it is important to bear in 328 mind that readily available nitrogen from manure is 5 times greater in spring compared to autumn 329 since more intense and recurring rainfall allows for a greater magnitude of redox potential (E_h) and 330 subsequently a higher magnitude of N₂O emissions.

331 <Figure 3B>

332 Fig. 3C compares the observed and simulated values of N₂O emissions for the threefour treatments 333 and the<u>including</u> control for the spring at NW. The magnitude of N_2O emissions varied between 334 0-20 g N/ha/d for the control, but between 0-200 g N/ha/d for the treatments. The latter reflected 335 the CS applications of 77.4 kg-N/ha in both treatments. The FYM treatment received an 336 application of 144 kg N/ha but the emission was in the same range as the control since readily 337 available nitrogen in FYM is only 0.67 kg N/ha compared to 43.5 kg N/ha for the CS treatment. 338 The readily available nitrogen in manure is 20% greater in spring at NW compared to spring at 339 PW. As the N_2O emission depends on the rainfall intensity, initial soil moisture and temperature, 340 application rate, timing, and frequency, the magnitude of simulated peak N_2O emission under the 341 CS-SB and CS-TS treatments was greater (200 g N/ha/d) during the spring at NW than the 342 magnitude (140 g N/ha/d) during the spring at PW. Furthermore, the rainfall during the spring at PW is less intense and erratic compared to spring at NW. In the case of the FYM treatment during
the spring at PW and NW, the average N₂O emission remains within 2-5 g N/ha/d, but the N₂O
emission during the spring at PW (Fig. 3C) is more erratic than during spring at NW (Fig. 3C).
This may be due to the erratic patterns of rainfall, soil temperature, and WFPS (%).

347 Regarding the mismatch between daily observed and simulated N₂O emissions, there are multiple 348 reasons including the irregular intervals of the empirical data for soil WFPS and soil temperature 349 and the impact of delayed bacterial activity due to daily corresponding temperature and/or rainfall 350 events. During a specific day, the optimum range of soil WFPS and soil temperature favours 351 biogeochemical processing due to nitrification and denitrification and subsequently N₂O 352 emissions. The magnitude of emissions again depends on the fertilizer (organic/inorganic) rate. It 353 means that if the soil WFPS and soil temperature are not within the optimum range, the bacterial 354 activity slows down and results in an underestimation/ overestimation for the simulated N₂O 355 emissions. Actually, the UK-DNDC model works well for annual emission fluxes (cumulative 356 daily emissions), compared to daily emissions, due to the reasons mentioned above. Bearing the 357 above in mind, the calibration and validation of annual emission fluxes under the different 358 treatments, locations, and weather conditions, shows acceptable statistical performance (Table 4). 359 <Figure 3C>

Generally speaking, UK-DNDC generally over-predicts daily N₂O fluxes for <u>the CS</u> treatment.

The UK-DNDC model was calibrated by fitting the stress coefficient of manure (S_{mn}) in the main nitrifier and denitrifier equations, which are one of the main drivers for optimizing annual N₂O emissions and peaks. Table 4 presents the results for the calibration and validation periods at PW. The R² is above 0.5 under all treatments during autumn (calibration) and all treatments, except CS-TS, during spring (validation), which suggested that simulated and observed annual N₂O emissions 366 wereare in good agreement. Similarly the RMSE was predicted to be below 0.62 (having R²>0.5
 367 in most cases) under all treatments during the autumn (calibration) and all treatments except CS 368 SB and CS-TS during spring (validation).

369 <Table 4> 370

371 **3.3.** Annual nitrous oxide emissions and emission factors

372 Many national and international reports, such as the annual IPCC report forof GHGs report total 373 emissions including seasonal and annual values rather than high resolution estimates. Therefore, 374 UK-DNDC was also calibrated (during the autumn season at PW) and validated (during the spring 375 season at PW) for annual N_2O emissions. Fig. 4 shows simulated and observed annual N_2O 376 emissions under the CS-SB, CS-TS, and FYM treatments for the autumn and spring at PW and the 377 spring at NW. The simulated emissions were relatively higher than the observed data in the case 378 of the CS-SB (2.31 kg-N/ha/y versus observed 0.80 kg-N/ha/y), and CS-TS (2.33 kg-N/ha/y versus 379 1.20 kg-N/ha/y) treatments for spring at PW. In all other treatments, the model overestimated the 380 annual emissions for the CS applications by 10-20% compared to the observed data, while it 381 underestimated the emissions for FYM. This may be because the observed data is not available for 382 the non-growth period in the winter and we used trapezoidal interpolation for the annual 383 cumulative emissions, resulting in an overestimation bias.

The highest observed emission is from FYM for the autumn and spring seasons at PW (1.28 kg-N/ha/y, 1.277 kg-N/ha/y, respectively) due to the erratic rainfall patterns (Dobbie et al., 1999). The nitrogen loading (144 kg-N/ha/y) is greatest during the spring season at NW compared to autumn (131 kg-N/ha/y) and spring (122 kg-N/ha/y) at PW, but the erratic pattern of rainfall and WFPS at PW is more favourable than at NW. In addition, a higher soil pH value (>7) favours denitrification (Li et al., 1992), whereas a low pH (<5.6) strongly inhibits soil microbial nitrification and denitrification (Wang et al., 2013). The R² for the controls treatments ranged from 0.01 in the 391 spring season at PW (Fig. 3B(a)) to 0.17 in the autumn season at PW (Fig. 3A(a)), while the R^2 392 for the other treatments ranged from 0.01 (CS-SB applied during the spring season at PW, (Fig. 393 3B(c)) to 0.17 (CS-SB applied during autumn season at PW, Fig. 3A(c)). Potential The R reasons 394 for theof lower value of correlation coefficients forin some treatments can include: (1) the daily 395 N₂O emission is strongly correlated with corresponding daily temperature and rainfall (Giltrap et 396 al., 2010). It also meanings that these climatic parameters are strong drivers of nitrous oxide 397 emissions without depending on the measured day, and; (2) the bacterial activity is delayed for 398 several days due to the temperature and rainfall events and corresponding temperatures but is then 399 and stimulateds due to an increase in temperature.

400 The modelled N₂O fluxes treated with CS-SB and CS-TS for the autumn and spring seasons at 401 PW and for the spring season at NW were higher than the observed valuesones (Fig. 6) because 402 the modelled peak values were more numerous and higher (Fig. 3A©, 3A(d), 3B©, 3B(d), 3C©, 403 3C(d), but thean opposite trend was observed in the other treatments experiments (Fig. 3A(b), 404 3B(b), 3C(b) (i.e. the modelled N₂O fluxes for the spring and autumn seasons at PW treated with 405 FYM, and for the spring season at NW treated with FYM were lower than the observed ones). The 406 over and under predictions of observed annual N₂O emissions using the UK-DNDC model reflect 407 the irregular intervals of observation, soil WFPS and the soil temperature status at a specific day 408 and time.

409 <Figure 4>

Using eq.1 (Fig. 6) and modelled data, $EF_{\underline{S}}$ for FYM and CS at the two sites were also calculated. The modelled EF exceeded the observed $EF_{\underline{S}}$ except for the FYM treatment during the autumn and spring seasons at PW and the spring season at NW. The IPCC Tier 1 default (EF=1%) underestimated the observed EF (<1%) in all cases except the CS-SB treatment during the autu

season at PW, and overestimated the simulated $EF_{\underline{s}}$ (1% > EF < 2%) for all cases except FYM during the autumn and spring seasons at PW and the spring season at NW. One of the reasons is that the some values of the observed emissions were negative (Fig. 3B, 3C), whereas modelled emission values produced by UK-DNDC were <u>all</u> positive (Myrgiotis et al., 2016). The both negative and positive values offset each other. Another reason is that, the UK-DNDC model produced many sharp and narrow peaks at low emissions in <u>the</u> case of the FYM treatment (Fig. 3A(b), 3B(b), 3C(b)), which contributed smaller percentages to the overall modelled emissions.

- 421
- 422
- 423

424 **3.4.** Effect of nitrogen loading rates on annual nitrous oxide emissions and EFs

425 Optimized fertilizer applications can mitigate N₂O emissions from grazing lands. N₂O emissions, 426 with respect to fertilizer N input, depend on location, climate, crop type, fertilizer type, soil 427 properties, N_2O emission measurement period, N input rates, biomass yield, cumulative N_2O 428 emissions and the N_2O EF. Kim et al., (2013) applied four different levels of N inputs based on 429 the 26 published datasets. These experimental sites were distributed globally in Canada, USA, and 430 Europe. Their application rates on grassland are almost the same factor $(1.5 \times \text{ and } 2 \times)$. Therefore 431 we used scenarios for FYM and CS by increasing by factors of 1.5 and 2 times the experimental 432 loadings at the two study sites (Table 2) (Kim et al., 2013; Shen et al., 2018). The annual N_2O 433 fluxes increased as a result of increasing the fertilizer loadings (CS and FYM) at both sites (Fig. 434 5). The response of the N_2O emissions as a function of nitrogen loading was similar in the case of 435 CS-SB and CS-TS, as wasned the gradual change (almost constant) due to the smaller percentage 436 of readily available nitrogen in FYM compared to CS for the spring and autumn seasons at PW 437 and the spring season at NW. The different scenarios of nitrogen loading forecasted the simulated

438 emission fluxes and <u>a</u> regression model between nitrogen loading and emission fluxes w<u>asere</u>
439 developed (Eq. 6).

440 <Figure 5>

441 The fitted constants "a" and "b" for the scenario analysis and the corresponding linear lines are 442 shown in Table 5 and Fig. 5, respectively. All of the coefficients of determination (R^2) exceeded 443 0.99 (Table 5), which indicates that the N₂O emissions increase linearly with increasing nitrogen 444 loading. The projected constants (EFs) (Table 5) were much lower than 0.01 (1%) in most of the 445 cases except the CS-SB and CS-TS treatments during the spring season at PW. The maximum EF 446 was 2% for CS under the trailing shoe application method applied during the spring season at PW, 447 and the minimum EF was 0.002% for FYM applied during the spring season at NW. The annual N₂O fluxes as a function of nitrogen loading are strongly ($\mathbb{R}^2 \approx 1$) dependent on each other in all 448 449 cases. For every 50 kg-N/ha/y of nitrogen loading, there was an increase of 0.5 kg-N/ha/y in the simulated annual N₂O emissions, which shows 1% emission flux in almost all cases except the 450 451 FYM treatment, as shown in Figure 5. This response is due to the slower rate of degradation of 452 FYM compared to CS.

453 <Table 5>

According to Kim et al., (2013), the relationship between N input and direct N_2O emissions follows three successive phases using the optimal N uptakes of both vegetation and soil microbes as boundaries. As N input initially increases (phase I), the N provided is consumed by plants and microbes, and N_2O emissions are primarily controlled by plant vs microbial competition for the available N. Therefore, in phase I, direct N_2O emissions increase linearly. Subsequently, as N additions exceed optimal N plant uptake rates, phase II would exhibit exponential increases of direct N2O emissions, since soil N_2O production increases rapidly with excess N supply. Finally,

as N additions continue to increase progressively beyond the capacity of soil microbes to take up 461 462 and utilize N (Phase III), the rate of N_2O production would slow down and reach a steady state. 463 Accordingly, the N input ranges of phases I, II, and III may change. If the N input range of phase 464 I is larger than the tested range of N input, it would appear to be a linear response of direct N₂O 465 emission and N input as verified in Figure 5. of the manuscript. In contrast, if the N input range of 466 phase I is smaller than the tested range of N input, an abrupt increase in direct N₂O emissions 467 would occur inside the tested range of N input and it would appear as an exponential response of 468 direct N_2O emissions with N input, as reported by fitted well by Kim et al., (2013).

The optimal N uptakes of both vegetation and soil microbes may change depending on vegetation type, climate conditions (e.g. temperature, precipitation) and soil properties (e.g. Ph, redox potential, soil aeration, organic and mineral N, amount and availability of C, texture, mineralogy–). All these conditions used in this manuscript are different from those used in the study by Kim et al., (2013); therefore, regression models can be fitted well using both linear and non-linear models, depending on optimal N uptake by both vegetation and soil microbes at the locality in question.

476 **3.5. Effects of N loading timing, dose and times on daily N₂O fluxes**

Fig. 6 shows the correlation coefficients between observed annual N₂O emissions and three dynamic variables including TPFA, daily rainfall, and daily air temperature under the three treatments, including the control, CS, and FYM for autumn and spring at PW and spring at NW. The N₂O emissions occurs due to the nitrification and denitrification processes, which are strongly related with these dynamic variables (Smith et al., 2003). The Arrhenius equation causes these chemical reactions to occur and N₂O emissions depend on temperature and soil aggregation (Smith et al., 2003). The variable WFPS does not take part directly in the reactions; however, the 484 completion of these reactions depends on soluble substrates and oxygen as required by 485 microorganisms. Under all casestreatments (control, CS, and FYM), and for both the spring and 486 autumn seasons at PW and the spring season at NW, the variable air temperature shows positive 487 and rainfall negative correlation coefficients. Whereas, tThe third variable, TFPA, 488 exhibited represents the negative correlation under all treatments and seasons at both PW and NW. 489 This shows that with the increase of TFPA, the soil N content will decrease, which is logical.-and 490 makes sense. Based on the positive and negative magnitude of correlation coefficients betweenof 491 TFPA, rainfall and temperature, it can be concluded that N₂O emissions at both research farms 492 increases with the increase of temperature and decreases with the increase of magnitude of rainfall 493 and TFPS.

494 <Figure 6>

3.6. Effect of scheduled and unscheduled fertilizer application on nitrous oxide emissions

496 The optimization of fertilizer input requires scheduled (split application during the growing 497 season) and precise fertigation based on the required nitrogen in the soil under different crop 498 physiological stages (Moore et al., 1996). These frequent but scheduled doses, according to the 499 crop physiological stages, significantly reduce peaks and overall emissions compared to a one-500 time (unscheduled) application of fertilizer (Table 3). The optimum timing of organic fertilizer 501 applications should not affect the silage quality, marginal profit, and grazing livestock. In order to 502 quantify the reduction in peaks using both methods, the CS-TS treatment was selected for the 503 autumn and spring seasons at PW and the spring season at NW (Fig. 7). The reason is that readily 504 available nitrogen (RAN) in FYM is present in a smaller percentage compared to CS, which will 505 take longer to degrade and be available to plants. The reduction in peak fluxes (schedule vs 506 unscheduled) was 85% for the autumn season at PW (Fig. 7(a)) and 50% for spring at PW (Fig.

507 7(b)) and NW (Fig. 7(c)). The overall annual N₂O emissions (schedule vs unscheduled) decreased
508 by 17% and 15% for the autumn season at PW and the spring season at NW, respectively
509 (Lassaletta, 2014, Pires et al., 2015). On the other hand, these emissions can also show increases,
510 such as an increase inof overall annual emissions by 9% in the case of the spring season at PW.
511 This makes sense as N₂O emissions are a function of air temperature, precipitation, and TPFA.

512 In practice, it is well realized that fertilizer best management practices (BMP) should utilize the 513 4R principle (Right source, Right rate, Right time, and Right place). This is embodied in Nutrient 514 Stewardship addressing the right fertilizer source, at the right rate, the right time, and in the right 515 place (IFA, 2007; Lassaletta et al., 2014; Wang et al., 2016). However, although at a first glance, 516 this best management appears simple, it is, in fact, complex with respect to considering how to 517 split nitrogen applications according to plant growth stages, especially in the context of ambient 518 weather and soil conditions. Our results showed that NUE could be much improved by changing 519 from low frequently split to high frequently split applications, such as changing from 1 time to 4 520 times. However, the corresponding improvement in NUE decreases if the frequency of split 521 applications is even higher, as reported by Cardenas et al (2019). Cardenas et al., (2019) compared 522 N₂O emissions associated with 4 split applications of inorganic fertilizers (AN320) with 6 split 523 applications (AN320-split) (in their Fig. 4 and Table 2). However, it is important to note here that 524 the times of the additional 2 applications were very close compared with the 4 time application 525 scenario. Since both split application scenarios reported by Cardenas et al. (2019) were high 526 frequency, their results did not show any significant effects of the number of split applications on 527 N₂O emissions.

528 Atmospheric CO_2 enrichment could inhibit the assimilation of nitrate into organic nitrogen 529 compounds (Bloom et al., 2010). The DNDC model takes into account the atmospheric

530 background CO₂ concentration with a default value of 350 ppm, which affects plant 531 photosynthesis. Also, according to Bloom et al., (2010), the concentration of CO_2 in the earth's 532 atmosphere ranges between 280 and 390 ppm, which confirms that the default value used in DNDC 533 is within this reported range. It is predicted that this concentration will reach between 530 and 970 534 ppm by the end of 21st century. Within this range of CO₂ concentrations, plant photosynthesis 535 behaves normally and therefore, there is no significant impact on N₂O emissions. Of course, if this 536 concentration doubles, as predicted by Bloom et al., (2010), the response of higher plants to a CO₂ 537 doubling would be a decline in nitrogen status. Overall, this means that the frequency of split 538 applications of organic/inorganic fertilizers according to crop physiological stages would likely decrease the emission rate and overall emissions (Reich et al., 2018). 539

540 Some comparisons between organic and inorganic sources of nitrogen showed the influence of 541 fertilizer types on N₂O flux (Cardenas et al., 2019; Shen et al., 2018; 2020; Thomas and Hao, 542 2017). Cardenas et al., (2019) concluded that these emissions depend on the type and rate of N 543 applied. For organic fertilizers, readily available nitrogen is much less than that reported for 544 inorganic fertilizers; therefore, the emission rate, overall emission and emission factor (EF) is 545 much lower than for inorganic fertilizers. Even within different forms of organic fertilizer such as 546 cattle manure, digestate, and separated solids, the emission rate varies. For example, Thomas and 547 Hao (2017) concluded that liquid biogas residues have a higher risk for N_2O emissions than both 548 the separated solid fraction of the biogas residues and undigested cattle manure. Similarly, Shen 549 et al., (2018; 2020) modelled N_2O emission following application of farmyard manure and green compost. The results showed that organic fertilizers applied to soils may increase nitrous oxide 550 551 emissions due to their lower C/N rations, and therefore potentially contribute to global warming.

552 It was further concluded that N_2O emission is mainly related to air temperature, precipitation, as 553 well as the time period between fertilizer application and sample measurement.

554 Keeping in view the reduction in peaks and overall emissions compared to one-time 555 applications, it was concluded that scheduling compared to one-time applications per season 556 (unscheduled) is an important factor for sustaining soil and water productivity, and reducing N_2O 557 emissions for environmentally-friendly smart agriculture and for contributing to a climate change 558 mitigation strategy. Therefore, our results are not in conflict with those reported by Cardenas et 559 al. $\frac{2}{3}$ (2019). Our results imply there is an optimal number of split applications. Our model can be 560 helpful to determine additional nitrogen needs. Timeliness of application is essential to be sure 561 plant yields do not suffer from nitrogen deficiency.

562 <Figure 7>

563 **4. Conclusions**

564 Organic fertilizers such as FYM and CS, are increasingly applied in agriculture because of the 565 benefits they provide in terms of plant nutrients, and soil quality. However, the varying 566 compositions of organic fertilizers, causes difficulties for precision fertilizer management. 567 Therefore, it is still a challenge to plan organic fertilization, such as timing, frequency, and dose 568 in site-specific conditions. In this study, the UK-DNDC model was applied to grazing grasslands 569 treated with FYM, CS-SB, and CS-TS treatments typical of intensive grassland farming in the UK. 570 The use of frequent low dose applications compared to one time amendments significantly reduced 571 N₂O peaks, fluxes and overall emissions by 17% for CS-TS during autumn at PW and 15% for CS-TS during spring at NW, but increased emissions for CS-TS by 9% during spring at PW. It is 572 573 therefore concluded that organic amendments scheduling compared to a traditional one-time 574 application per season can be a useful on-farm mitigation measure for minimizing N_2O emissions.

The application of liquid manure in modern agriculture is one of the most important techniques for controlling overall N_2O emissions and fertilizer use efficiency, and this study demonstrates how the integration of empirical and modelling data can be used to help design the optimum use of farm organic manures and slurries.

579

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809	List of Tables	

811 Table 1. Soil, vegetation, and climatic parameters along with manure application rates for four different treatments
 812 including control, cattle slurry surface broadcast, cattle slurry trailing shoes, and farmyard manure during autumn
 813 and spring seasons at PW and the spring season at NW, UK.
 814

- [#] both autumn and spring seasons at PW*autumn season at PW (Source: Nicholson et al., 2017)
- **spring season at PW (Source: Nicholson et al., 2017)
- ^{\$}spring season at NW (Source: Cardenas et al., 2010)

Table 2. Loadings of nitrogen and carbon applied to grassland under two different treatments (cattle slurry and farmyard manure) during autumn and spring at PW and spring at NW.

N and C loading by			Treatment		
vydysite	Site	C& of Brol	CS-SB	ESMS	FYM_
Bartinumbe PW	PW [#]	52.3526 ⁰ N	52.3526 ⁰ N	52.3526 ⁰ N	52.3526 ⁰ N
Factor**	NW 1	50.77 03 5⁰N	5 0 .77035 ⁰ N 1	50.77035P.N	50.7 <u>7</u> 035 ⁰ N
Kongitude (kg-N/ha/v)	$PW_{24}^{\#}$	3.7977 ₃₆ W	$\frac{3}{48}$ ^{7977°W} 131	3.7977 ⁰	$3.787^{\circ}W$
C loading (kg-N/ha/y)	NW_{48}	3.901072°W	3,901072° W	3.901072^{0} W	$3_{3}\overline{9}0\overline{1}072^{0}W$
Soil texture	-10	Clay lóấm	Clay loam ¹⁷⁰³	Clay foam	Clay loam
Clay (%)	PW [#]	28	28	28	28
Spring PW	NW	29	29	29	29
Danisity (g/cm ³)	PW^* 1	0.95 1.5	0295 1	0.95 1.5	0.952
N loading (kg-N/ha/y)	PW_{67}^{**}	$0.9_{100.5}$	1949 122	0.9 183	0.2_{44}
C loading (kg-N/ha/y)	NW ₁₃₄	$0.68_{-}201_{-}$	268^{68} 1586	0.68 2379	03682
Soil NO ₃ (mg/kg)	PW ^{#*}	5.15	-5.15	5.15	5.15
	NW	0.36	0.36	0.36	0.36
SeffnSH1™(mg/kg)	PW [#]	2.22	2.22	2.22	2.22
Factor	NW 1	0.65 1.5	0265 1	0.65 1.5	0.652
Arkaning (kg)N/ha/y)	P₩ [#] 7.4	4.7116.1	154.187 144	4.7 216	4.288
C loading (kg-N/ha/y)	NW 4.8	3.65232.2	309 <u>3</u> 6 ⁵ 1872	3.65 2808	³ 3944
Soil pH	PW,NW	5.6	5.6	5.6	5.6
Ann. Rainfall (cm)	PW [*]	143	143	143	143
	PW	203	203	203	203
	NW DUV*	148	148	148	148
Annual Ave. Temp.	PW*	0.00	0.00	0.00	0.00
(°C)	D11/**	9.88	9.88	9.88	9.88
	PW	9.1	9.1	9.1	9.1
a .	NW ³	10.21	10.21	10.21	10.21
Cropping	D11/*	Grassland	Grassland	Grassland	Grassland
Manure. App.	PW*	0	24	24	101
Rate(kg-N/ha)	D11/**	0	24	24	131
	PW**	0	67	67	122
	NW DUU*	0	77.4	77.4	144
Date fertilized	PW*	NA	Sep 28,2011	Sep 28,2011	Sep 28,2011
	PW ^{***}	NA	May 2,2012	May 2,2012	May 2,2012
	NW	NA	Apr. 17,2012	Apr. 17,2012	Apr. 17,2012

 829 830 831 832 833 834 *The default values of the C/N ratio for cattle slurry and farmyard manure are 2 and 13, respectively. 	
 830 831 832 833 834 *The default values of the C/N ratio for cattle slurry and farmyard manure are 2 and 13 respectively. 	
 831 832 833 834 835 *The default values of the C/N ratio for cattle slurry and farmyard manure are 2 and 13, respectively. 	
 832 833 834 835 *The default values of the C/N ratio for cattle slurry and farmvard manure are 2 and 13 respectively. 	
 833 834 835 *The default values of the C/N ratio for cattle slurry and farmvard manure are 2 and 13, respectively. 	
834 *The default values of the C/N ratio for cattle slurry and farmvard manure are 2 and 13, respectively.	
*The default values of the C/N ratio for cattle slurry and farmvard manure are 2 and 13, respectively.	
**The nitrogen loading factor <u>was taken fromhas been used following</u> Kim et al., (2013). PW-Pwllpeiran NW-North Wyke 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 877 888 859 860 861 862 863 864 865 866 877 888 859 860 861 862 863 864 865 866 877 888 859 860 861 862 863 864 865 866 877 888 859 860 861 862 863 864 865 866 867 868 866 867 868 866 867 868 866 867 868 866 867 868 866 867 868 869 860 861 862 866 867 868 866 867 868 866 867 868 866 867 868 866 867 868 866 867 868 866 867 868 866 866	cation and
split applications (according to crop physiological stages) during autumn and spring at PW and spring at	NW

	Total RAN [*] kg N/ha	Split1 kg N/ha	Split2 kg N/ha	Split3 kg N/ha	Split4 kg N/ha
Autumn, PW	9.4	1.63	1.35	1.63	4.80
Application Date		April 5,2011	April 15,2011	April 30,2011	May 20,2011
Spring, PW	35	6.06	5.01	6.06	17.88
Application Date		April 5,2011	April 15,2011	April 30,2011	May 20,2011

Spring,NW	43.5	7.53	6.22	7.53	22.22
Application Date		May 12,2012	May 22,2012	07-Jun-12	29-Jun-12

867 * Readily available nitrogen868

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Table 4: Statistical measures including coefficient of determination (R²), root mean square error (RMSE), absolute
error (AE), and relative error (RE), for comparing between observed and simulated annual nitrous oxide emissions
under the different treatments during the calibration (autumn and spring at PW in 2011) and validation (spring at
NW in 2012) periods.

	Control	CS-SB*	CS-TS**	FYM***
Autumn PW (Calibration)				
^a Obs.N ₂ O	0.78	1.03	0.99	1.28
^a Sim.N ₂ O	0.99	1.41	1.42	1.00
\mathbb{R}^2	0.81	0.54	0.89	0.96
RMSE	0.24	0.48	0.62	0.61
AE ^a	0.22	0.39	0.53	0.54
RE(%)	28.04	37.47	43.27	-21.56
Spring PW (Validation)				
^a Obs.N ₂ O	0.57	0.80	1.20	1.28
^a Sim.N ₂ O	1.09	2.31	2.33	1.10
\mathbb{R}^2	0.74	0.39	0.01	0.97
RMSE	0.60	1.52	1.18	0.42
AE ^a	0.52	1.51	1.13	0.29
RE(%)	91.65	188.28	93.81	-14.22

875 * cattle slurry treatment using surface broadcasting method

876 ** cattle slurry treatment using trailing shoe method

877 *** farmyard manure

- 878 ^a Annual average nitrous oxide flux (kg-N/ha/y)
- 879 880

Table 5. The regression coefficients in equation (6) during the scenario analysis for nitrogen loadings under <u>the</u>

cattle slurry surface broadcast (CS-SB), cattle slurry trailing shoe (CS-TS), and farmyard manure (FYM) treatments
 during <u>the</u> autumn season at PW, spring season at PW, and spring season at NW.

CS-	CS-	FYM	CS-	CS-	FYM	CS-	CS-	FYM
SB	TS		SB	TS		SB	TS	
Autumn			Spring			Spring		
 PW			PW			NW		

	a	0.0179	0.0182	8.00E-05	0.02	0.0204	3.E-05	0.0173	0.0174	2.E-05
	b	0.9176	0.9208	0.9351	0.9616	0.952	1.0782	0.0899	0.078	0.2841
	R ²	1	0.9998	0.9999	0.9998	0.9998	0.9966	0.9999	0.9999	0.9999
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Figure 2A. Temporal variation of rainfall during autumn at PW (a), spring at PW (b), and spring at NW (c). Similarly tTemporal variation of simulated (solid line) and observed (dots) WFPS (water filled pore space) during autumn at PW (d), spring at PW (e), and spring at NW (f).





929 Figure 2B. Temporal variation of air and soil temperature during autumn at PW (a), spring at PW (b) and spring at NW (c).

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Figure 3A. Temporal variation of simulated (solid line) and observed (dots) nitrous oxide flux
under the control (a), FYM (b), CS-SB (c), and CS-TS (d) treatments during autumn at PW. Here,
FYM stands for farmyard manure, CS-SB for cattle slurry application using the surface broadcast
method, and CS-TS for cattle slurry application using the trailing shoe method.



Figure 3B. Temporal variation of simulated (solid line) and observed (dots) nitrous oxide flux
under the control (a), FYM (b), CS-SB (c), and CS-TS (d) treatments for spring at PW. Here, FYM
stands for farmyard manure, CS-SB for cattle slurry application using the surface broadcast
method, and CS-TS for cattle slurry application using the trailing shoe method.



Figure 3C. Temporal variation of simulated (solid line) and observed (dots) nitrous oxide flux
under the control (a), FYM (b), CS-SB (c), and CS-TS (d) treatments for spring at NW. Here, FYM
stands for farmyard manure, CS-SB for cattle slurry application using the surface broadcast
method, and CS-TS for cattle slurry application using the trailing shoe method.





993 994 Figure 4: Observed and simulated annual nitrous oxide fluxes and emission factors (EFs) for the 995 cattle slurry surface broadcast treatment (CS-SB) during the autumn (CS-SB1) and spring (CS-996 SB4) seasons at PW and the spring season (CS-SB7) at NW, .- Ffor the cattle slurry trailing shoe 997 (CS-TS) treatment during the autumn (CS-TS2) and spring (CS-TS5) seasons at PW and the spring

season (CS-TS8) at NW<u>and</u>. Similarly for the farmyard manure (FYM) treatment during the autumn (FYM3) and spring (FYM6) seasons at PW and the spring season (FYM9) at NW. The error bars indicates the standard deviations among replications of each treatment.



Figure 5: Predicted annual nitrous oxide fluxes with respect to increasing nitrogen loading under
the cattle slurry surface broadcast (CS-SB), cattle slurry trailing shoe (CS-TS), and farmyard
manure (FYM) treatments during the autumn at PW (a), spring at PW (b), and spring at NW (c).
Similarly cCorresponding emission factors (EFs) during the autumn at PW (d), spring at PW (e),
and spring at NW (f).





Figure 6: Linear correlation coefficients <u>betweenof</u> the observed N₂O emissions <u>andwith</u> TPFA, rainfall (R), and average air temperature (T) under the control, cattle slurry and farmyard manure (FYM) treatments during the autumn at PW (Au-PW), spring at NW (Sp-NW), and the spring season at PW (Sp-PW). <u>Under cattle slurry treatment</u>, the linear correlation between N₂O emissions and TPFA, R, and T. Similarly under farmyard manure (FYM) treatment the linear correlation between N₂O emissions and TPFA, R, and average air temperature. The error bars indicates the standard deviation among replications of each treatment.





Figure 7: Comparison of nitrous oxide fluctuations after one time split (black line) and four times split (red line) split-organic fertilizer applications under the cattle slurry treatment during the autumn at PW (a), spring at PW (b), and spring at NW (c).

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