The challenge of modelling nitrogen management at the field scale: simulation and sensitivity analysis of N_2O fluxes across nine experimental sites using DailyDayCent

2014 Environ. Res. Lett. 9 095003

(http://iopscience.iop.org/1748-9326/9/9/095003)

OPEN ACCESS
IOP Publishing
Environmental Research Letters
Environ. Res. Lett. **9** (2014) 095003 (15pp)
doi:10.1088/1748-9326/9/9/095003

The challenge of modelling nitrogen management at the field scale: simulation and sensitivity analysis of N_2O fluxes across nine experimental sites using DailyDayCent

N Fitton[1], A Datta[1,6], A Hastings[1], M Kuhnert[1], C F E Topp[2], J M Cloy[2], R M Rees[2], L M Cardenas[3], J R Williams[4], K Smith[4], D Chadwick[5] and P Smith[1]

[1] Institute of Biological and Environmental Sciences, University of Aberdeen, 23 St. Machar Drive, Aberdeen AB24 3UU, Scotland, UK
[2] SRUC Edinburgh, West Mains Road, Edinburgh EH9 3JG, UK
[3] Rothamsted Research, North Wyke, Okehampton, Devon EX20 2SB, UK
[4] ADAS, Battlegate Road, Boxworth, Cambridge CB23 4NN, UK
[5] School of Environment, Natural Resources and Geography, Bangor University, Deiniol Rd., Bangor, Gwynedd LL57 2UW, UK
[6] Center for Environmental Studies, Earth Sciences and Climate Change Division, The Energy and Resources Institute, Barbaru Seth Block, India Habitat Center, New Delhi 110003, India

E-mail: n.fitton@abdn.ac.uk

Received 27 May 2014, revised 25 July 2014
Accepted for publication 25 July 2014
Published 8 September 2014

Abstract

The United Kingdom currently reports nitrous oxide emissions from agriculture using the IPCC default Tier 1 methodology. However Tier 1 estimates have a large degree of uncertainty as they do not account for spatial variations in emissions. Therefore biogeochemical models such as DailyDayCent (DDC) are increasingly being used to provide a spatially disaggregated assessment of annual emissions. Prior to use, an assessment of the ability of the model to predict annual emissions should be undertaken, coupled with an analysis of how model inputs influence model outputs, and whether the modelled estimates are more robust that those derived from the Tier 1 methodology. The aims of the study were (a) to evaluate if the DailyDayCent model can accurately estimate annual N_2O emissions across nine different experimental sites, (b) to examine its sensitivity to different soil and climate inputs across a number of experimental sites and (c) to examine the influence of uncertainty in the measured inputs on modelled N_2O emissions. DailyDayCent performed well across the range of cropland and grassland sites, particularly for fertilized fields indicating that it is robust for UK conditions. The sensitivity of the model varied across the sites and also between fertilizer/manure treatments. Overall our results showed that there was a stronger correlation between the sensitivity of N_2O emissions to changes in soil pH and clay content than the remaining input parameters used in this study. The lower the initial site values for soil pH and clay content, the more sensitive DDC was to changes from their initial value. When we compared modelled estimates with Tier 1 estimates for each site, we found that DailyDayCent provided a more accurate representation of the rate of annual emissions.

Keywords: DailyDayCent, nitrous oxide emissions, sensitivity and uncertainty analysis, Monte–Carlo simulations, UK croplands and grasslands

1. Introduction

Despite its relatively low atmospheric concentration, nitrous oxide (N_2O) is an extremely important greenhouse gas (GHG) with a global warming potential of nearly 300 times that of CO_2. Concentrations of N_2O in the atmosphere have increased to 324 ppb, which is approximately 20% higher than pre-industrial level (Stocker *et al* 2013). Natural and managed soils are one of the principal sources of N_2O, and increasing pressure for food production has led to enhanced N inputs via fertilizer application. This, in turn, has led to an increase in N_2O emissions (Jones *et al* 2007, Reay *et al* 2012). Recent estimates suggest that, despite a small decrease, total N_2O emissions in the United Kingdom (UK) in 2010 were approximately 112 Kt N_2O–N, with emissions from agricultural soils accounting for 77.5% of the total emissions (National Atmospheric Emissions Inventory, 2013). The UK is a signatory of the United Nations Convention on Climate Change (UNFFCC) and is obliged to reporting anthropogenic sources of GHG's in a national inventory. Current reporting methods are based on updated methodologies developed by the Intergovernmental Panel on Climate Change (IPCC). For N_2O emissions from soils, Tier 1 default reporting assumes that between 0.3 and 3% of any synthetic N applied to the soil is re-released as N_2O–N (IPCC 2006). However, this methodology tends to produce a relatively large uncertainty of total emissions as it does not a) account for spatial variations in emissions, or b) allow for the inclusion of mitigation options other than those affecting total N application (Abdalla *et al* 2010, Saggar *et al* 2007). Process-based models such as DailyDayCent (DDC) have been considered for simulating GHG emissions across a range of different ecosystems and climate zones. Use of these models aim to improve inventory reporting to Tier 2 or 3 levels, which could potentially reduce the uncertainty in total emissions, and adequately reflect N_2O emission reduction through nitrogen management.

Prior to their use, an assessment of the suitability of the model to simulate the GHG of interest is required, by comparing modelled emissions with measured values. This should preferably include a wide range of experimental sites reflecting the range of climate, soil and management types represented within a country. However, uncertainty in measured inputs used to drive biogeochemical models can lead to uncertainty in modelled outputs, due to the sensitivity of the model to changes in inputs. Therefore, an understanding of how input uncertainty can propagate through the model, and the interactions between inputs is essential (Ogle *et al* 2003, Hastings *et al* 2010, Del Grosso *et al* 2010, Fitton *et al* 2014). The aims of the study were (a) to evaluate if the DailyDayCent model can accurately estimate annual N_2O emissions across nine different experimental sites (cropland and grassland with a range of climate, soil and different rates and types of nitrogen (N) fertilizer or manure application), (b) to examine its sensitivity to different soil and climate inputs across a number of experimental sites and (c) to examine the influence of uncertainty in the measured inputs on modelled N_2O emissions.

2. Materials and methods

2.1. Experimental sites

Emissions of N_2O (treatment replicate number (n) = 3) were measured at six cropland experimental sites; Boxworth, Terrington, Betley, Middleton, and two Gleadthorpe sites: Grange Field and Lamb Field using the static chamber method (Chadwick *et al* 2014). The sites selected represent N_2O emissions from a range of different soil, climate, fertilizer types and rates were used across the cropland sites. Table 1 outlines the key soil and climate characteristics, crop type, fertilizer type and dates and rates of N application. More specific details on the experimental design for each site are outlined in Smith *et al* (2011) and Dampney *et al* (2006)

The Boxworth and Terrington experimental sites were sub-divided into four plots with four treatment types; a control and plots with ammonium nitrate (AN), urea ammonium nitrate (UAN) and urea applied. The Betley and Middleton experimental sites were split into a control and manure application plots, and both the Grange and Lamb Field experimental sites were sub-divided into six plots, where there was an increasing target AN fertilizer application rate (table 1(a)). Emissions of N_2O were also measured from three grazed grassland sites: Crichton, Rowden and Debath. As with the cropland sites, each grassland site was sub-divided into a control and different fertilizer treatments, details of which are outlined in table 1(b).

2.2. DailyDayCent model overview and validation

DailyDayCent (DDC) is a daily time-step version of the Century model which simulates the fluxes of C and N between the atmosphere, soil and vegetation (Parton *et al* 1998). The key sub-models in DDC include soil organic matter pools (SOM), microbial pool, the water budget, leaching and soil temperature sub-model, as well as a N sub–model. DDC also includes plant growth with dynamic C allocation among the above- and below-ground biomass pools. Soil carbon is distributed in a microbial pool and three SOM pools that have three distinct decomposition rates, where C and N fluxes are simulated through the plant litter and organic pools (Parton *et al* 1998). In addition, N_2O fluxes are controlled by soil NH_4^+ and NO_3^- concentrations, water content, temperature, gas diffusivity and labile C availability (Parton *et al* 1998). DDC uses a daily time-step, which is controlled by a scheduling file where fertilization, harvest and tillage events are scheduled for the dates when they occurred

Table 1. Soil, climate and management information for each of the (a) cropland and (b) grassland experimental sites used in this study.

Site name	Experiment period	Temperature[a]	Precipitation[a]	Soil pH	Bulk density	Soil type	Crop type	Fertilizer types	Amount of fertilizer applied[d]
(a) Cropland		°C	mm		g cm^{-3}				
Boxworth	9/3/2005–21/9/2005	10.1	556	8.2	1.2	Calcareous clay	Winter wheat	Control, AN, UAN, urea[b]	160 kg N yr^{-1} (40, 60, 60)
Terrington	1/3/2004–17/2/2005	10.8	672	8.1	1.38	Silty clay loam	Winter wheat	Control, AN, UAN, urea[b]	220] kg N yr^{-1} (40, 90, 90)
Betley	4/11/2004–18/10/2005	10.1	625	6.5	1.09	Sandy loam	Winter wheat	Control, cattle slurry (C/N = 15)	113 kg N yr^{-1} (113)
Middleton	5/4/2005–4/4/2006	9.6	769	7.5	0.93	Silty clay loam	Winter wheat	Control, pig slurry (C/N = 20)	48 kg N yr^{-1} (48)
Grange Field	27/2/2008–10/3/2009	9.5	625	6	1.12	Sandy silt loam	Winter wheat	Control, 70, 140, 210, 280, 350[c]	
Lamb Field	19/2/2007–4/3/2008	9.4	645	5.8	1.42	Loamy sand	Winter barley	Control, 70, 140, 210, 280, 350[c]	
(b) Grassland									
Crichton	10/3/2004–26/1/2005	8.9	1079	6.3	1.3	Sandy loam	Grass	Control, AN, UAS, urea	220 kg N yr^{-1} (40, 80, 100)
Rowden	2/3/2004–9/2/2005	10.1	1039	6.1	1.2	Silty clay loam	Grass	Control, AN, UAS, urea	300 kg N yr^{-1} (40, 80, 100, 80)
Debathe	28/2/2005–2/9/2005	10.1	1039	6.7	1.6	Coarse sandy loam	Grass	Control, AN, urea	120 kg N yr^{-1} (40, 80)

[a] Long term average.
[b] AN is Ammonium nitrate, UAN is urea ammonium nitrate and UAS is urea ammonium sulphate.
[c] Indicates a target application rate of *x* kg of ammonium nitrate applied per hectare per year.
[d] Values in brackets indicate the rate of fertilizer applied on the first, second, third or fourth application dates.

during the experimental period and also, if required, over the preceding years.

Due to the differences in climate, soil and historic land management, modelled estimates of N_2O for each site differed from each other, especially in response to the timing and type of management. However, for each site DDC was calibrated by initially establishing soil carbon (C) equilibrium. This was then followed by a period of appropriate crop or grassland management with nitrogen (N) input, such as fertilizer application, to ensure that soil mineral N was not a limiting factor during the pre-experimental period. This was then followed by site-specific management for the time period prior to and including the experimental measurements, where site specific information was available. Other than site-

Table 2. Soil and climate variables and the range each is to be varied from the site value which acts as the mid-point.

Parameter to be varied	Uncertainty range[a]	Number of steps to be simulated
Daily temperature (°C)	+/−1 °C	10
Daily precipitation (mm)	+/−1 mm	10
Soil pH (pH unit)	+/−1 pH unit	10
Clay content (%)	+/−20%	10
Bulk density (g cm^{-3})	+/−0.2 g cm^{-3}	10

[a] Values here are derived from Fitton *et al* (2014).

specific management and site inputs, only crop parameters such as genetic growth potential (PRDX) were adjusted at each site to reflect observed above ground productivity, and these were then left unchanged between the experimental plots (Fitton *et al* 2014). The model was applied across all sites with no further calibration, so that any differences in model outputs were driven only by site inputs. Modelled daily and annual N_2O emissions were then compared to the corresponding measured values, and these were termed the baseline N_2O emissions. This was repeated for crop yields, where measured values were available.

2.3. Sensitivity and uncertainty analysis of key input variables

The key input parameters (table 2) and their uncertainty range, and the methods of performing the sensitivity and uncertainty analysis used here are adapted from those described in Fitton *et al* (2014). For each soil and climate input, we assumed a normal distribution in the uncertainty range and the percentage or absolute range for each input was the same for each experimental site. By using the site value as the median point we then simulated a ten step-wise change in each site input. Where for each step, only a single soil input was varied while the remaining inputs were held at the original site value. With regards to the climate inputs, DDC uses daily climate information; therefore, the uncertainty values of 1 °C or 1 mm refers to uncertainty in daily values and only values over the experimental period were changed. Using Monte–Carlo simulations, we then tested the potential influence of uncertainties in the soil and climate inputs on modelled N_2O emissions. To do this, we assumed each input and its range of values had an equal weight and that each was independent of other variables. We then sub-sampled 10,000 unique combinations of all inputs over their uncertainty ranges and simulated daily and annual N_2O emissions (Fitton *et al* 2014).

2.4. Statistical analysis

At each experimental site and plot, we tested model performance by calculating; the root mean square error (RMSE) compared to the measured 95% confidence interval, relative error (E) compared to the measured 95% confidence interval ($E_{95\%}$) and mean difference, M (assessed by the $t_{2.5\%}$ statistic) between the modelled, the mean measured and replicate N_2O fluxes, as described in detail in Smith *et al* (1997) and Smith and Smith (2007). Following this, we calculated the variance in the modelled daily N_2O fluxes in the ten datasets generated as part of the sensitivity analysis. We then applied the best fit regression equation, using Minitab™, to the baseline N_2O fluxes derived using the original site inputs. This allowed an assessment of how uncertainty in each input propagates through the model, or more specifically, if the uncertainty propagation is linear or nonlinear (data not shown; Hastings *et al* 2010, Fitton *et al* 2014).

The importance of uncertainty in each input parameter on the range of output simulated values, as arising from the Monte–Carlo simulations was calculated by determining the contribution index (%) according the formula (Vose 2000):

$$c_i(\text{contribution index}) = \frac{\sigma_g - \sigma_i}{\sum_{i=1}^{i_{max}}(\sigma_g - \sigma_i)} \times 100$$

Where c_i is the contribution index (%) in factor i, σ_g is the standard deviation in the total uncertainty (across the Monte–Carlo simulations), σ_i is the standard deviation of the range of values simulated as part of the sensitivity analysis of each input, i, where i is the specific input of interest at the time, and i_{max} is the total number of model input factors considered. The higher the percentage value, the more important is the input. The contribution index was calculated for each study site and their experimental treatment plots.

2.5. Tier 1 calculations

Tier 1 annual N_2O emissions from each experimental plot were calculated as the product of the annual amount of nitrogen (N) in crop residues and the total amount of N applied to the soil multiplied by the default emission factor. The N content of crop residues were calculated using default values detailed in the IPCC guidelines (IPCC 2006) and the fraction of residue removed annually for animal feed, bedding and construction for the UK (82%) was the same assumed by Smith *et al* (2000). This was then added to the quantity of N fertilizer or organic additions, and the total N was multiplied by the default emission factor (0.01 kg N_2O–N ha^{-1} yr^{-1}), and the uncertainty range between 0.003 and 0.03 kg N_2O–N ha^{-1} yr^{-1} (IPCC 2006).

3. Results

3.1. Site simulations

(a) *Cropland sites*:

Results of the statistical analysis used to test the model performance in simulating daily N_2O fluxes are summarised in table 3(a). While each test was performed separately for each site and plot, for ease of presentation values here represent the average for each experimental site. In plots with no, or a low rate of, N applied the correlation between daily modelled and measured N_2O fluxes was relatively poor. For

Table 3. The performance of the DailyDayCent model in simulating N2O emissions for each fertilizer type across all (a) cropland and (b) grassland experimental sites. Association is significant for $t > t$ (at $P = 0.05$). Model bias is not significant for $E < E95$. Error between measured and modelled values is not significant for $F < F$ (critical at 5%).

(a) Croplands	Boxworth	Terrington	Middleton	Betley	Grange Field	Lamb Field
R^2	0.43	0.52	0.08	0.42	0.50	0.27
RMSE	246.65%	133.88%	204.07%	113.68%	108.56%	131.76%
RMSE (95% Confidence limit)	641.44%	633.49%	698.96%	350.61%	202.02%	275.46%
t value for M	−5.29	0.93	−0.70	1.50	1.44	0.16
t value for M at $p = 0.05$	1.97	1.97	2.01	2.00	1.97	1.97
E	−92.51	7.95	−20.77	22.55	9.74	1.36
E (95% Confidence limit)	458.23	394.16	594.89	273.08	145.24	206.33

(b) Grasslands	Crichton	Debathe	Rowden
R^2	0.44	0.12	0.19
RMSE	143.70%	423.31%	212.79%
RMSE (95% Confidence limit)	644.37%	1670.70%	889.06%
t value for M	−3.97	−2.01	0.70
t value for M at $p = 0.05$	1.97	1.98	1.97
E	−38.73	−84.41	10.17
E (95% Confidence limit)	423.01	626.86	364.76

example, in the Terrington and Boxworth control plots, the coefficient of determination of the linear regression was $R^2 = -0.01$ and $R^2 = 0.14$, respectively. The exception to this was the Betley experimental site, where modelled estimates correlated well with measured values. As N application rates increased, the correlation coefficient improved. In addition, across all plots and sites, when replicate measured values were considered there was no statistically significant total error (RMSE) or bias (M with t-test) when compared to measured estimates (table 3(a)).

The average rate of annual N_2O emissions across all cropland sites was 2 kg N_2O–N ha^{-1} yr^{-1} (standard deviation: 1.03 kg N_2O–N ha^{-1} yr^{-1}). The highest rate of annual N_2O emissions was recorded at the Gleadthorpe Lamb Field experimental plot (3.8 kg N_2O–N ha^{-1} yr^{-1}) with a fertilizer application rate of 350 kg N ha^{-1} yr^{-1}. The lowest measured annual N_2O emissions were recorded at the Middleton control plot (0.41 kg N_2O–N ha^{-1} yr^{-1}). DailyDayCent was able to provide a good estimate of annual emissions of N_2O and a reasonable estimate of crop yields across the six cropland experimental sites. For N_2O emissions there was a 50:50 split between over or underestimation of annual N_2O emissions (figure 1(a)), showing that any error is not systematic. In sites such as Boxworth and Terrington which had a higher pH, average annual temperature and clay content relative to the other sites, DDC tended to underestimate average annual emissions. In the other sites, which are characterised by lower clay contents, DDC tended to overestimate average annual N_2O emissions. Yield estimates were also collated for each of the experimental sites. As with N_2O fluxes, yield values were also variable due to the variation in the amount and type of N applied. The highest yield of either winter wheat or winter barley was measured at the Boxworth AN experimental plot (9.86 Mg ha^{-1}) and the lowest yield was measured in the Terrington control plot (4.68 Mg ha^{-1}). DDC was able to provide a reasonable estimate of annual yields (figure 1(b)), with R^2 values between modelled and measured values lower than for N_2O estimates. Overall DDC tended to underestimate low yields, but provided better simulation of higher yields.

(b) *Grassland sites*:

As with the cropland sites, the correlation between measured and modelled N_2O fluxes was poor in the control plots (table 3(b)). For some sites (e.g. Debathe), even when N-fertilizer was applied, there was still a poor correlation between measured and modelled N_2O fluxes. This was primarily due to periods of estimated uptake of N_2O from the atmosphere, a process not included yet in any process-based model. DDC therefore simulated a very low rate of N_2O emissions over the same period. Despite these discrepancies, there was no statistically significant total error (RMSE) or bias (M with t-test) when compared to measured estimates.

The average annual emissions across all the grassland experimental plots were of a similar magnitude to croplands at 2.9 kg N_2O–N ha^{-1} yr^{-1}. The highest measured annual emissions was 8.2 kg N_2O–N ha^{-1} yr^{-1} recorded in the Rowden AN experimental plot. The lowest annual values indicated there was an uptake of −0.14 kg N_2O–N ha^{-1} yr^{-1} at the Debathe control plot. The standard deviation in the range of values was also higher than across all the cropland sites at 2.89 kg N_2O–N ha^{-1} yr^{-1}. With the exception of the Rowden control and AN experimental plots, DDC tended to overestimate N_2O emissions. However, when we directly compared all modelled and measured annual N_2O emissions across all plots (figure 1(c)) the correlation coefficient (R^2) was 0.84. Yield estimates were not available for the grassland sites.

3.2. Sensitivity analysis

(i) *Variation in model sensitivity by site*

(a) *Cropland sites*

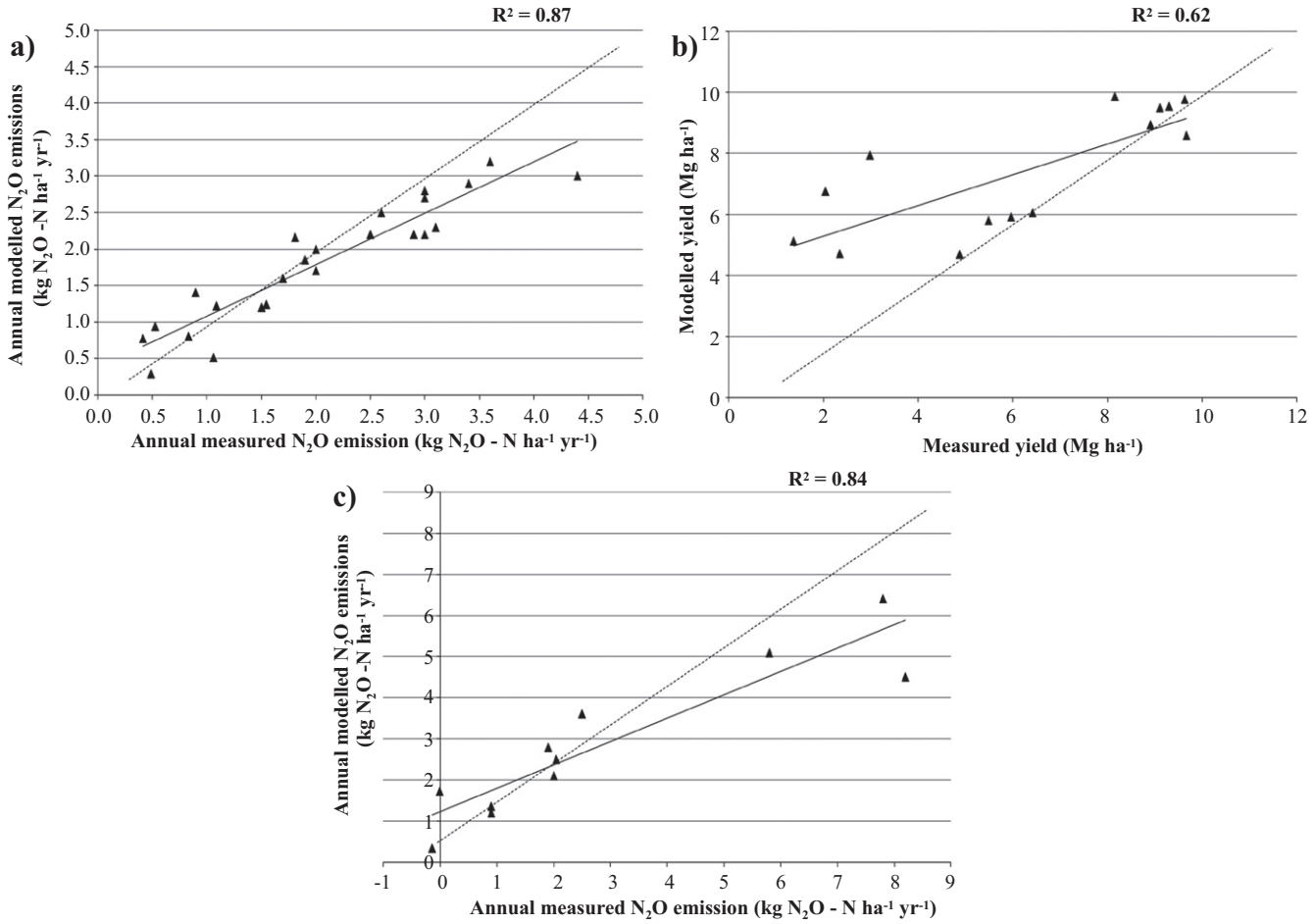

Figure 1. Represents 1:1 plots between the modelled and measured estimates of: annual N2O emissions (a) and crop yields (b) across the 6 UK experimental sites and annual N_2O emissions in the across the three UK grassland experimental sites (c). R^2 values represent the regression coefficient.

Table 4(a) outlines the range of modelled estimates for the six UK cropland sites, simulated during the Monte–Carlo simulations. For ease of presentation here the upper and lower ranges here represent the average of simulated values that were higher or lower than baseline annual emissions. For all cropland sites, changes in site inputs tended to cause an increase in annual emissions when compared to baseline estimates. For example, at the Boxworth experimental site, 79% of the unique combinations generated as part of the Monte–Carlo simulations led to an increase in annual emissions. When averaged across all sites an average of all uncertainty around modelled N_2O emissions was approximately 25%, with this value varying significantly between sites, fertilizer treatment and crop type in the range of 6–48%. For example each plot at the Terrington experimental site had the lowest range of annual emissions, simulated as part of the Monte–Carlo simulations, with baseline emissions changing by between 7 and 12%. Changes to modelled annual emissions at Gleadthorpe—Lamb Field experimental site were the highest, with annual emissions varying by between 30 and 48% across the Monte–Carlo simulations.

As expected, the contribution index of the different site inputs to uncertainty in annual emissions varied among the experimental sites and with the type of fertilizer applied. As with the statistical analysis, values presented here represent the average for each cropland site (figures 2(a)–(f)). For modelled estimates of N_2O fluxes at the Boxworth control plot, bulk density accounted for 89% of the range of N_2O emissions simulated across the Monte–Carlo simulations. Precipitation was the least important factor accounting for only 2%. Where fertilizer was applied, the percentage contribution of bulk density decreased. Despite a still significantly smaller contribution, precipitation became the second most important factor, accounting for between 11 and 15% of the range of annual N_2O emissions (figure 2(a)). In all plots at the Terrington experimental site, precipitation and bulk density were the most important contributors to changes in annual emissions (figure 2(b)). However, where no N-fertilizer was applied, precipitation was found to be the most important factor followed by bulk density, with the reverse being true for estimates where fertilizer was applied. In addition, as the type of fertilizer changed from AN to UAS then Urea the percentage contribution of precipitation and bulk density decreased.

When averaged across all plots at the Betley experimental site, precipitation, bulk density, soil pH and clay

Table 4. (i) The baseline annual emissions modelled using site level inputs and the average of the annual N_2O emissions that were higher (upper range) or lower (lower range) than baseline estimates simulated across the Monte–Carlo simulations, (ii) the average, maximum and minimum annual N_2O emissions measured at each experimental site. Values are for (a) cropland and (b) grassland sites and the units expressed are in kg N_2O–N ha^{-1} yr^{-1}.

	Experimental site		Modelled annual N_2O emissions (kg N_2O–N ha^{-1} yr^{-1})			Measured annual N_2O emissions (kg N_2O–N ha^{-1} yr^{-1})		
			Lower range	Baseline	Upper range	Minimum	Baseline	Maximum
(a)	Boxworth	Control	0.20	0.20	0.26	0.33	0.50	0.63
		AN[a]	0.74	0.80	1.31	0.51	0.89	1.40
		Urea	1.13	1.20	1.69	0.94	1.46	1.90
		UAN[a]	1.13	1.20	1.69	0.44	1.10	1.58
	Terrington	Control	1.14	1.20	1.30	1.20	1.50	1.70
		AN[a]	2.00	2.20	2.53	2.30	2.50	2.70
		Urea	2.15	2.20	2.68	2.40	3.00	3.90
		UAN[a]	2.59	2.80	3.17	3.00	3.00	3.20
	Betley	Control	0.48	0.51	0.70	0.60	1.06	1.70
		Manure	1.91	2.16	2.82	1.50	1.81	2.50
	Middleton	Control	0.69	0.77	0.88	0.30	0.42	0.50
		Manure	0.86	0.94	1.06	0.17	0.52	0.80
	Grange Field[b]	0	1.24	1.60	4.88	1.60	1.70	2.00
		70	1.52	1.85	5.26	1.70	1.90	2.30
		140	1.74	2.20	5.48	2.90	2.90	3.00
		210	2.19	2.50	5.76	2.30	2.60	2.90
		280	2.52	2.90	5.97	3.20	3.40	3.80
		350	2.85	3.20	6.29	3.30	3.60	3.90
	Lamb Field[b]	0	0.99	1.40	4.35	0.80	0.90	1.00
		70	1.21	1.70	4.67	1.80	2.00	2.20
		140	1.53	2.00	4.85	1.80	2.00	2.40
		210	1.89	2.30	5.06	3.10	3.10	3.30
		280	2.24	2.70	5.30	2.70	3.00	3.40
		350	2.57	3.00	5.50	3.80	4.40	4.80
(b)	Crichton	Control	1.14	1.14	1.26	0.50	0.90	1.20
		AN[a]	3.38	3.59	3.92	2.00	2.50	3.30
		Urea	2.60	2.79	3.09	1.10	1.90	2.90
		UAS[a]	2.38	2.49	2.68	1.90	2.04	3.10
	Rowden	Control	1.77	1.89	2.19	1.40	2.00	3.10
		AN[a]	4.08	4.51	4.43	4.70	8.20	11.10
		Urea	4.70	5.10	5.09	2.70	5.80	8.40
		UAS[a]	5.92	6.40	6.42	2.70	7.80	15.70
	Debathe	Control	0.37	0.34	0.46	−0.15	−0.14	−0.10
		AN[a]	1.14	1.36	1.60	0.40	0.90	1.50
		Urea	1.66	1.73	1.89	−0.03	−0.01	0.05

[a] AN is Ammonium nitrate, UAN is urea ammonium nitrate and UAS is urea ammonium sulphate.
[b] Indicates a target application rate of *x* kg of ammonium nitrate applied per hectare per year.

content accounted for an almost equal portion of modelled values (figure 2(c)). Temperature was the least important factor in modelled estimates regardless of manure application; however, the order of importance of the remaining inputs varied between both plots. Where manure was applied, the order of importance of the different inputs was: soil pH (25%), precipitation (24%), bulk density (24%) and clay content (23%). In the control plot, precipitation accounted for 44% followed by bulk density (24%) and soil pH (15%). Unlike other sites, at the Middleton experimental site there was no difference in the order of importance of the soil and climate inputs between modelled values at the control site and where manure was applied (figure 2(d)). Precipitation was found to be the most important factor, accounting for 44% of the range of modelled estimates followed by temperature (35%) and bulk density (18%). Both clay and soil

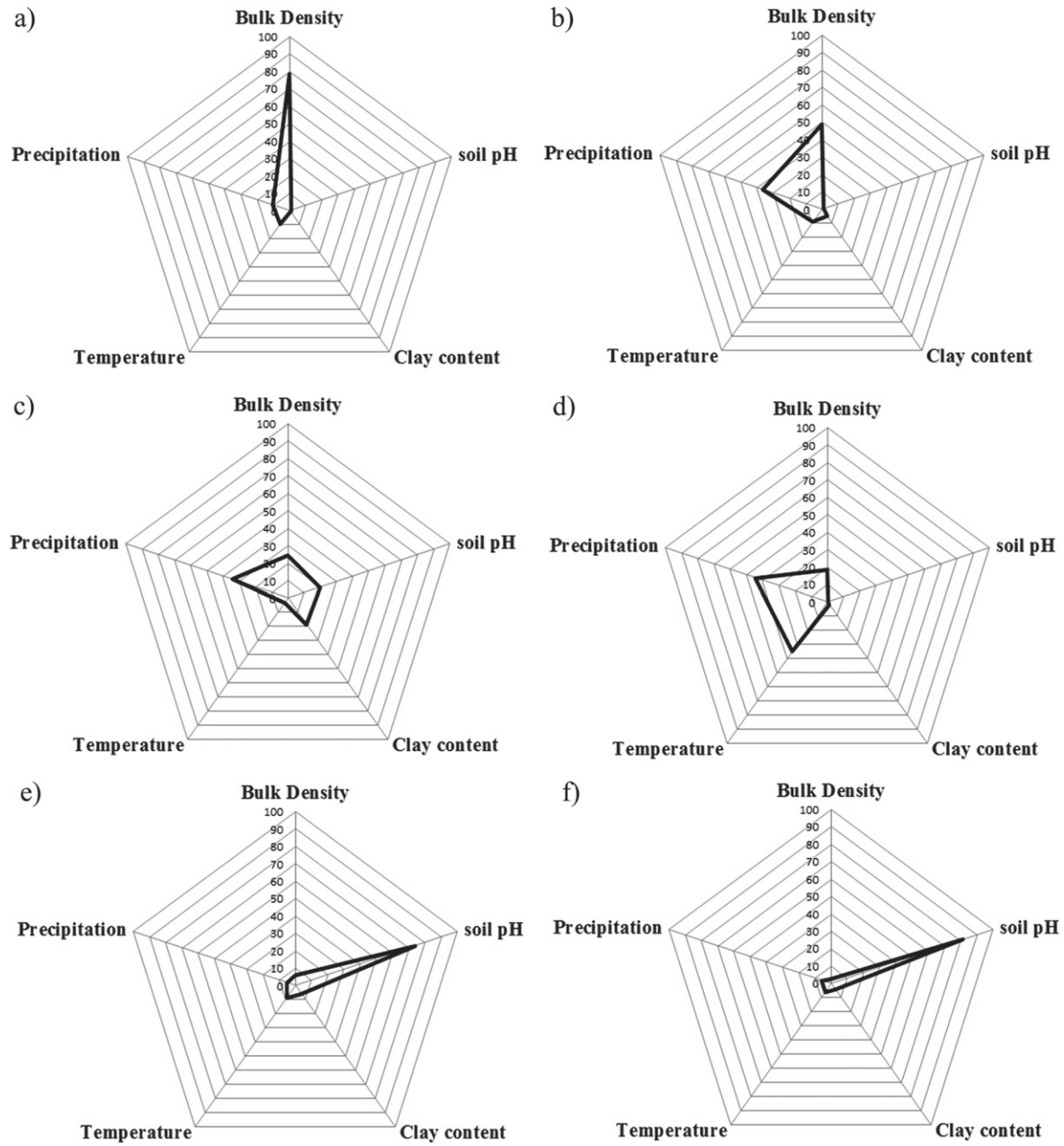

Figure 2. Contribution index: the contribution (%) of each soil and climate input to the range of annual N_2O emissions simulated after the Monte–Carlo simulations averaged across the control and fertilizer types for: (a) Boxworth, (b) Terrington, (c) Betley, (d) Middleton, (e) Grange Field and (f) Lamb Field cropland experimental sites. Values represent the normalized percentage change in the standard deviation of the range of annual N_2O emissions simulated after the sensitivity analysis of each individual input with respect to the standard deviation of the outputs from the Monte–Carlo simulations.

pH accounted for only approximately 2.5% of total uncertainty in both plots.

At the Gleadthorpe—Grange Field experimental site, pH is the single most important factor in our modelled estimates from the Monte–Carlo simulations (figure 2(e)). However, as the rate of N application increases, its percentage contribution decreases from 70 to 62%. The contribution of the remaining inputs differs depending on whether or not N is applied, but as indicated in figure 2(e), their contribution is relatively small. Soil pH is also the most important factor at the Lamb Field site (figure 2(f)), but unlike Grange Field, as the N application rate increased, the percentage contribution of soil pH remained relatively constant. In addition, after soil pH, the climate inputs provided a higher contribution to total uncertainty, whereas at the Grange Field experimental site the soil inputs were the three most important inputs driving the changes in modelled estimates.

(b) *Grassland sites*

Table 4(b) outlines the range of modelled estimates at the three UK grassland sites simulated during the Monte–Carlo simulations. The upper and lower ranges represent the average of values that are higher or lower than baseline annual

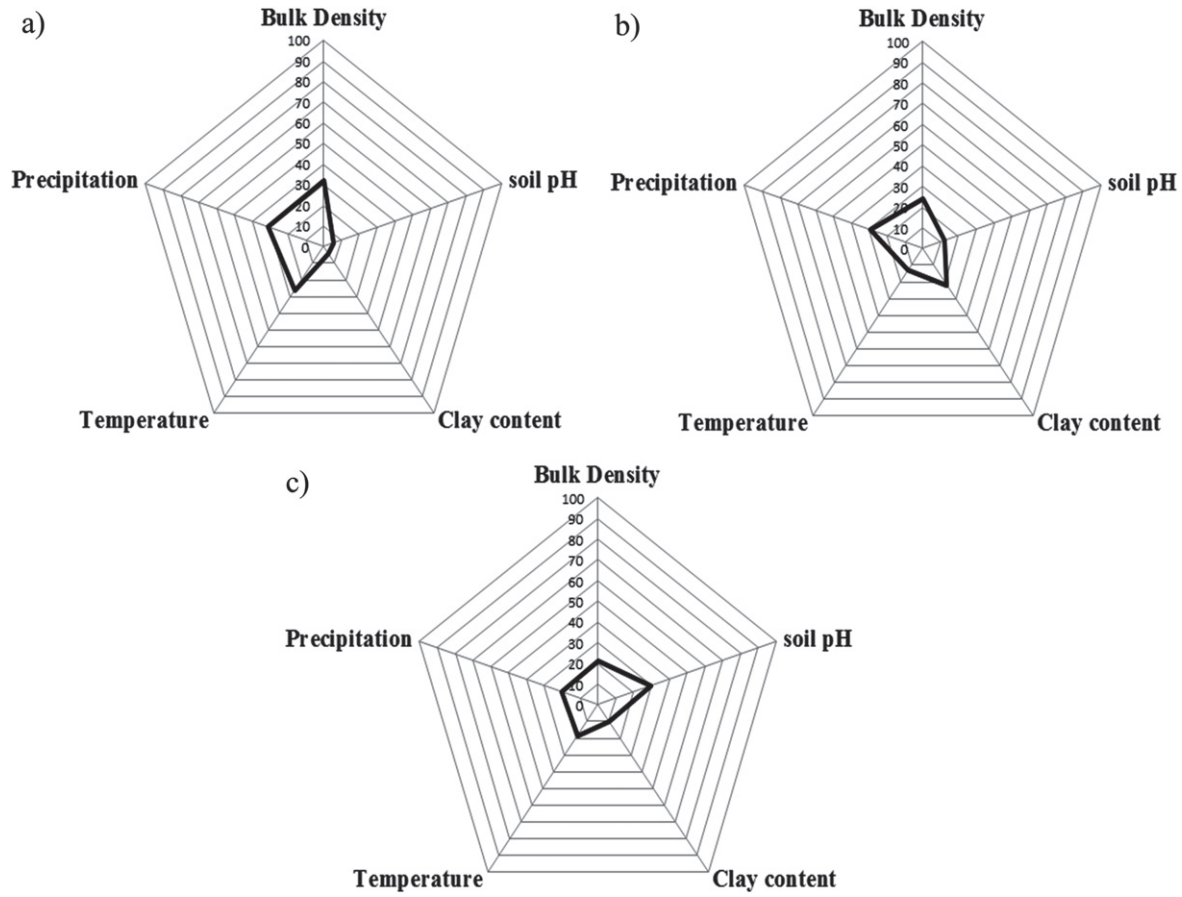

Figure 3. Contribution index: the contribution (%) of each soil and climate input to the range of annual N_2O emissions simulated after the Monte–Carlo simulations averaged across the control and fertilizer types for: (a) Crichton, (b) Rowden and (c) Debathe grassland experimental sites. Values represent the normalized percentage change in the standard deviation of the range of annual N_2O emissions simulated after the sensitivity analysis of each individual input with respect to the standard deviation of the outputs from the Monte–Carlo simulations.

emissions. Across the different grassland sites, baseline estimates at the Crichton site tended to fall in the middle of the range of values simulated across the Monte–Carlo simulations. In contrast, at the Rowden and Debathe experimental sites, baseline emissions fell in the upper range of values simulated.

When averaged across all plots at Crichton, precipitation, temperature and bulk density are the three most important inputs, with these accounting for 83% of the range of values simulated as part of the Monte–Carlo simulations (figure 3(a)). The order of the importance of these changed between the control and different N fertilizer plots i.e. the percentage contribution these three inputs always accounts for between 82 and 98% of the range of modelled emissions. Changes in bulk density, clay content and precipitation accounted for most of the range of annual N_2O emissions simulated at the Rowden experimental site (figure 3(b)). Where N-fertilizer was applied, precipitation and clay content tended to be the most important factors, accounting for between 56 and 63% of the variation in annual emissions between them. However, where no N was applied, bulk density and temperature were the most important factors. Changes in soil pH accounted for 42% of the change in emissions at the Debathe experimental site (figure 3(c)) followed by temperature, bulk density and precipitation. Unlike the other grassland sites, the order of the importance did not significantly change with N application, nor did the percentage contribution of these inputs to total uncertainty.

(ii) *Variation in the sensitivity by fertilizer type*

(a) *Cropland sites*

The contribution of the different inputs to uncertainty in annual emissions, across the experimental plots with the same type of fertilizer applied is outlined in figure 4. In the control plots there is an almost equal split in the importance of the different inputs: soil pH, bulk density and precipitation which contribute 30, 28 and 27% (figure 4(a)). In the experimental plots with UAN and Urea applied, bulk density was the most important factor accounting for 40 and 64% of the variation in the Monte–Carlo simulations (figures 4(c), (d)). This was driven by the sensitivity of DDC to changes in bulk density at the Boxworth experimental site. Soil pH is the most important factor for plots with AN applied, which accounts for 64% of the range of annual emissions (figure 3(b)). This importance is primarily due to the sensitivity of DDC to soil pH at the Grange and Lamb Field experimental sites. With regards to manure application, the precipitation and temperature were

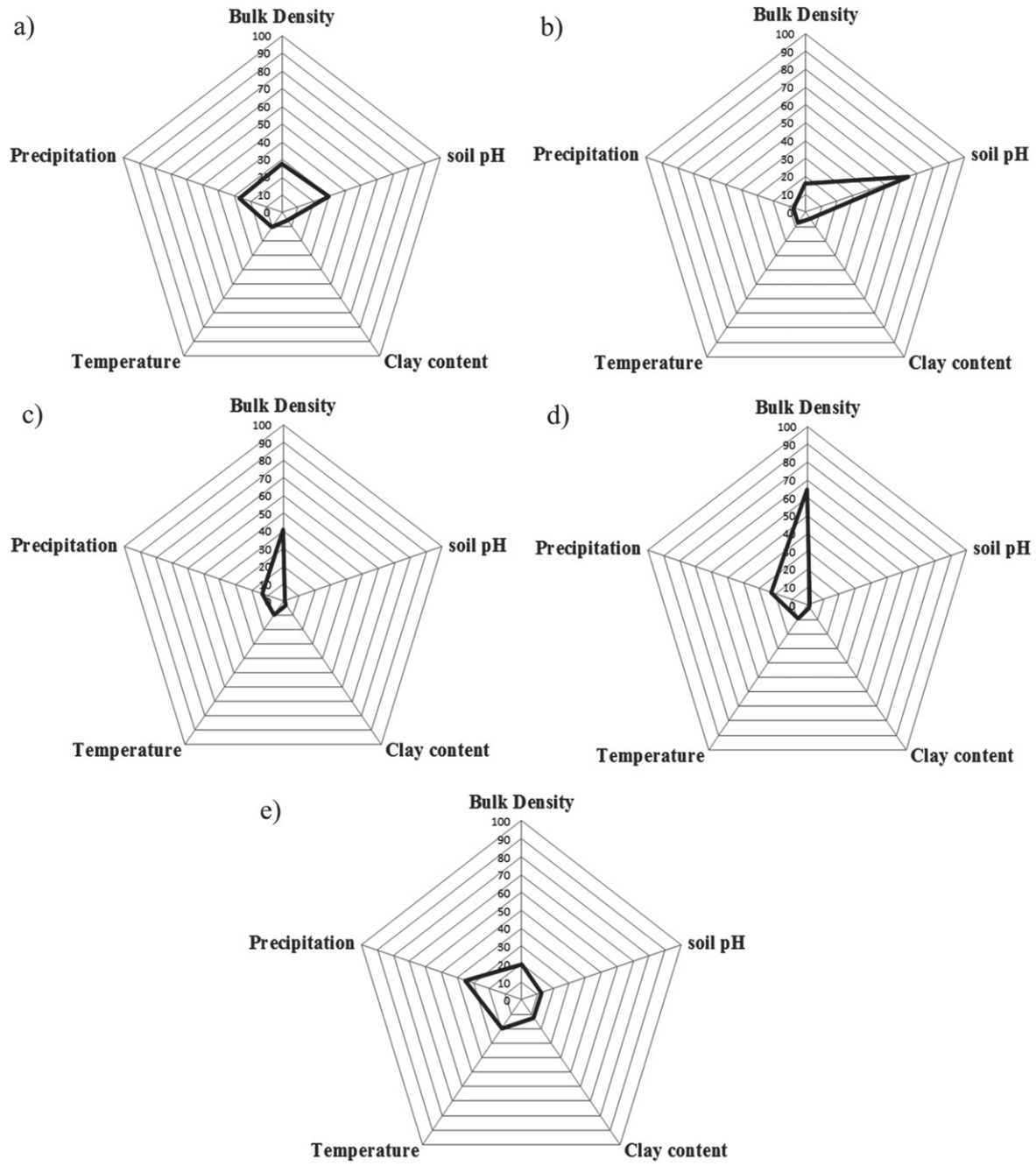

Figure 4. Contribution index: the contribution (%) of each soil and climate input to the range of annual N_2O emissions simulated after the Monte–Carlo simulations averaged across all the: (a) control, (b) AN, (c) UAN and (d) urea and (e) manure experimental plots in all sites. Values represent the normalized percentage change in the standard deviation of the range of annual N_2O emissions simulated after the sensitivity analysis of each individual input with respect to the standard deviation of the outputs from the Monte–Carlo simulations.

the most important factors in terms of total uncertainty. Overall, both climate inputs accounted for 35 and 19% of the total uncertainty; however, bulk density also contributed 18% of the uncertainty in modelled estimates (figure 4(e)).

(b) *Grassland sites*

The contribution of the different site inputs to uncertainty in modelled estimates are outlined in figure 5. Across all the control plots (figure 5(a)), bulk density was the most important factor accounting for ~40% of the variation in annual emissions simulated across the Monte–Carlo simulations. Soil pH was the least important factor accounting for only 8% of emissions, and the percentage contribution of the remaining inputs was roughly equal, at approximately 18%. Across the AN and UAS experimental plots, precipitation was the most important factor accounting for 33 and 40% of annual emissions. The order of importance of the remaining inputs differed, as in the AN plot, bulk density and temperature were the second and third most important factors, whereas across the UAS plots this order was reversed (figures 4.15(b), (c)). In the experimental plots with Urea application, soil pH was

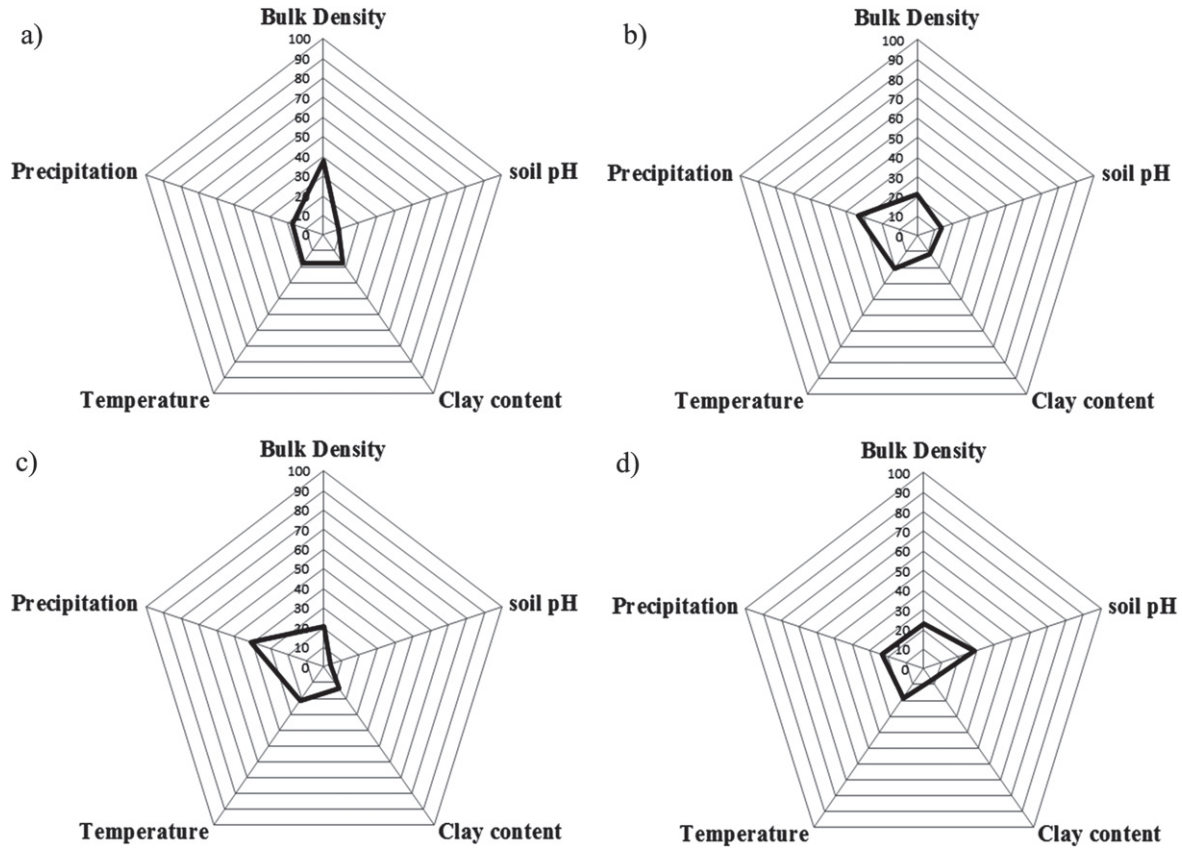

Figure 5. Contribution index: the contribution (%) of each soil and climate input to the range of annual N_2O emissions simulated after the Monte–Carlo simulations averaged across all the: (a) control, (b) AN, (c) UAN and (d) urea experimental plots in all grassland sites. Values represent the normalized percentage change in the standard deviation of the range of annual N_2O emissions simulated after the sensitivity analysis of each individual input with respect to the standard deviation of the outputs from the Monte–Carlo simulations.

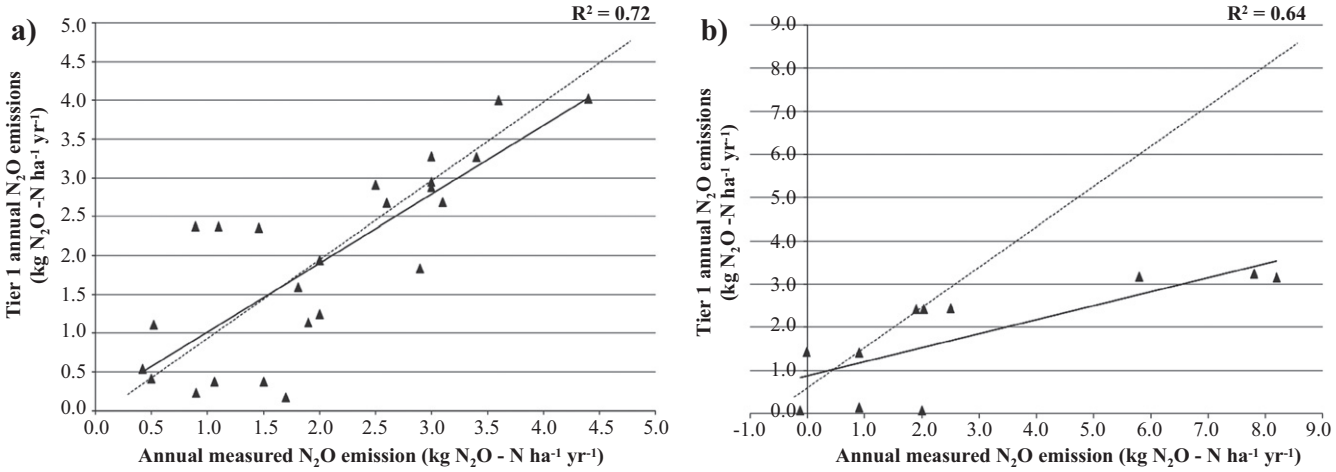

Figure 6. Represents a 1:1 plot between the measured and Tier 1 estimated annual N_2O emissions across the (a) six UK cropland experimental sites and plots and (b) the three UK grassland experimental sites and plots. R^2 values represent the regression coefficient.

deemed to be the most important factor accounting for 29% of the range in annual estimates. Precipitation (23%), bulk density (22%) and temperature (18%) were the next most important factors, where their percentage contribution to total uncertainty was of the same magnitude (figure 5(d)).

3.3. Tier 1 emission calculations

Figures 6(a), (b) represents a 1:1 plot between measured annual N_2O emissions and annual emissions calculated using the Tier 1 methods, and the default emission factor of 0.01 kg N_2O–N ha^{-1} yr^{-1} in all cropland and grassland experimental plots, respectively. For the cropland sites, Tier 1 emission

factors tended to underestimate annual emissions by an average of 32%, with the large differences occurring in estimated annual emissions in plots with no N applied. The regression coefficient (R^2) between measured and Tier 1 values was 0.65 (figure 6(a)). The exception to this was at the Boxworth sites (except for the control plot), the Terrington AN plot, both Middleton plots, the Grange Field 210 and 350 kg N ha^{-1} plots. Here annual emissions, as calculated using Tier 1 methodology, tended to be double the corresponding measured values. When we assumed that 0.3% of N applied is emitted, (lower uncertainty range), Tier 1 methodology underestimated annual emissions in all sites by an average of 70%. Where we assumed a 3% rate of emission (higher uncertainty range), Tier 1 methodology overestimated annual emissions by an average of 43%.

In the grassland sites, there was a 50:50 split between under or over-estimation of annual emissions using the Tier 1 method. This was because, at the Debathe experimental site and the control plot at each site, Tier 1 estimations were consistently higher. Whereas in the Rowden plot, Tier 1 estimations were consistently lower and at Crichton there was a 50:50 split (figure 6(b)). When we assumed 0.3% of N applied is emitted (lower uncertainty range), the Tier 1 methodology underestimated annual emissions by an average of 63%. The exception to this was the DeBathe control and Urea plots, where annual emissions were still overestimated. Where we assumed 3% of N applied is emitted (higher uncertainty range), the Tier 1 method consistently overestimated the corresponding measured annual values. The exception to this was the control plots at the Crichton and Rowden experimental sites.

4. Discussion

(a) *Site simulation*

This study aimed to test if the biogeochemical model DDC could accurately replicate N_2O fluxes across six cropland and three grassland experimental sites, with a range of soil, climate and management types. When all experimental plots, including (where available) comparisons with the yield estimates were considered, we can conclude that DDC provides a reasonable estimate of annual N_2O emissions within the UK. For some experimental plots, there was no statistically significant correlation in the pattern of emissions between modelled and measured values (expected at low emission rates). When other statistical tests and the variation in the measurements were considered, modelled emissions tended to show good agreement with measured values. However, there are a number of limitations in both the model processes and data availability that can cause differences in the magnitude and pattern of N_2O emissions. These limitations can lead to a difference in the modelled N_2O response to management events such as fertilizer application, or even precipitation events, and also feed into the sensitivity of the DDC model to changes in site inputs.

(i) *Limited site input information*

As stated in section 2.2, model validation requires both site level inputs and measured data against which modelled estimates can be compared. Although not detailed here, a full calibration of DailyDayCent, like all biogeochemical models, requires an extensive experimental dataset (Gottschalk *et al* 2007, Hastings *et al* 2010, Bell *et al* 2012). However, across the different experimental sites data availability varied. These included a lack of long term climate information and initial soil C stock values as inputs, or missing yield values from experimental plots for comparing against modelled values. This has been well documented in other studies that have undertaken crop modelling, especially on a larger spatial scale such as region or country level (Palosuo *et al* 2011, Rötter *et al* 2012). However measurement based experiments, especially those undertaken to inform national inventories, are increasingly considering model requirements as part of their experimental design.

(ii) *Rainfall when temperatures fall below zero degrees*:

As part of the input files used to run DDC, daily inputs of temperature and precipitation are used. In the DDC model, once the average daily temperature falls below zero degrees at the same time as a precipitation event, the model assumes that precipitation will fall as snow. Any increase in the average air temperature to above zero degrees is coupled with snow melt, and this can lead to a large 'pulse' in N_2O from the soil. For example, at the Middleton experimental plot towards the end of the calendar year, DDC modelled a large pulse of N_2O of approximately 35 kg N_2O–N immediately after a combination of sub -zero temperatures and a precipitation event. This has been observed in other modelling studies (de Bruijn *et al* 2009), but this pulse was not observed in the measured values, as the precipitation did not fall as snow as the model assumed.

(iii) *Direction of N_2O flux between soil and atmosphere*:

DDC assumes that at all times the concentration of N_2O is higher in soils than the atmosphere, so that there can never be a net uptake of N_2O from the atmosphere. Uptake of N_2O has frequently been reported in experimental studies (Butterbach-Bahl *et al* 2002, Syakila *et al* 2010), but the processes responsible for N_2O uptake remain poorly understood (Butterbach-Bahl *et al* 2013). At the Debathe experimental site, annual measured N_2O emissions indicated there was a slight uptake of N_2O of −0.01 and −0.14 kg N_2O–N, in the control and Urea plots, respectively. This was driven by a period during the experimental study when measured values consistently showed an uptake of N_2O. While modelled N_2O emissions over this period were low, there was always a net release of N_2O; therefore, over a 365 day period, there was up to a 180% difference between modelled and measured annual emissions.

(b) *Sensitivity of the DDC model to uncertainty in measured values*

The soil and climate inputs used to test the sensitivity of DailyDayCent were selected based on the site specific information available at all experimental sites. By using the same percentage or arbitrary change in each soil input in the sensitivity analysis we aimed to (a) reflect potential variation at a UK site level rather than on a larger spatial scale and (b)

investigate the sensitivity of the model both between and within the experimental sites, and determine the underlying causes of model sensitivity.

(i) *Sensitivity of DDC to changes in soil parameters*:

For some sites, changes in site level inputs led to a change in the initial soil C, where soil C increased or decreased from values simulated using site level inputs. The effect of this change differed between the sites. In some instances, this led to a change in both the pattern and magnitude of N_2O emissions from baseline estimates. For other sites, only the magnitude of daily emissions changed. For example, at the Boxworth experimental site, DDC was most sensitive to changes in soil bulk density. Here increasing bulk density led to a small increase in the initial system C during the spin up phase. This in turn led to the change in both the yield and N_2O emissions but both the pattern of emissions and daily crop growth remained unchanged. However only when bulk density was changed by 0.2 g cm^{-3} (i.e. maximum allowable) there was a slight change in pattern in both the pattern of emissions and crop growth. At the Betley experimental site, DDC was more sensitive to any change in soil pH. This is not unexpected as the baseline value of soil pH was relatively low. This meant that, unlike at Boxworth, the larger the change in soil pH, the more effect this had on modelled estimates. This could be seen via changes in estimated soil C and crop growth during the experimental year which in turn led to changes in water movement within the profile. Therefore the sensitivity of DDC to soil pH affected both the pattern and magnitude of emissions from the manure experimental plot.

(ii) *Sensitivity of DDC to changes in daily temperature and precipitation patterns*:

Changes in temperature and precipitation alter N_2O processes in a different manner to soil parameters, as both climate parameters were only changed over the experimental period. Plant production potential evapotranspiration rate (PET) and soil decomposition rates are controlled by moisture and temperature. In addition, if the data is unavailable, soil temperature is also estimated from daily temperature and soil moisture (Sansoulet *et al* 2014). Depending on the baseline climatic conditions, e.g. precipitation patterns in the experimental year, the effect on N_2O emissions varied between the sites. For example rainfall patterns at the Middleton experimental site meant that when rainfall occurred, it was relatively heavy and was over a few days. Reducing rainfall in the period up to and including this period meant that the soil was less saturated than baseline estimates. This caused an increase in N_2O emissions during these periods, as decreasing daily precipitation values from the baseline level soil moisture levels became more optimal for nitrification/denitrification. As a consequence peak emissions were higher than baseline estimates, especially at lower temperatures and after management events such as cultivation. Conversely, increasing daily precipitation values meant that, while emissions were lower after the management events, N_2O fluxes were higher in the earlier part of the year, which under normal conditions was drier. Therefore increasing daily precipitation, but not to a point where soil saturation occurs also led to an increase in daily emissions.

(iii) *Interaction of changes to total C and incorrectly simulated snow fall*:

The Grange and Lamb experimental sites were both based within the Gleadthorpe experimental area, and the same climate inputs were used for both sites. For each plot, in both experimental sites, N_2O exhibited the largest sensitivity to changes in soil pH. When soil pH was decreased from the site value, DDC simulated a higher soil C level during the spin-up phase. This was a similar response to changes in bulk density in Boxworth outlined above. However, the relatively large differences in N_2O emissions was due to a fall of the average air temperature below 0 °C towards the end of the experimental period, which was coupled with rainfall events. As discussed earlier, DDC assumed that the precipitation fell as snow (which it did not), which was then coupled by snow melt as temperatures increased, leading to a spike in simulated N_2O emissions. Freeze-thaw cycles have been shown to be important in contributing to episodes of N_2O emissions (Röver *et al* 1998, Teepe *et al*, Kurganova & de Gerenyu 2010) and various mechanisms have been used by models to represent the processes responsible (de Bruijn *et al* 2009). However in the UK, freezing is usually short lived and often results solely in the freezing of surface soil layers. For this reason the impact of freeze thaw cycles on N_2O emissions are likely to have been less important in the sites included in this study than assumed in the model. Over the experimental period, climate data used by DDC show a repeated pattern of decreasing then increasing temperature coupled with precipitation. When coupled with a higher rate of N_2O emissions due to higher soil C annual N_2O emissions, this can increase estimates in annual emissions (Fitton *et al* 2014).

(iv) *Sensitivity of DDC to interactions of increasing* fertilizer *application rate and* fertilizer *type*:

With the exception of the Gleadthorpe experimental sites, a range of different fertilizer types were used and within each site, there was a difference in the sensitivity of DDC to changes in the site level inputs. For example in the Terrington UAN experimental plot, changes in soil pH coupled with the application of UAN led to higher N_2O emissions relative to baseline emissions. However, for the AN and urea plots, which were fertilized on the same day, the same pattern was not repeated and N_2O fluxes remained unchanged. This was also observed at the Crichton experimental plot where, the pattern of both modelled and measured N_2O fluxes in the AN and urea plots differed in the experimental year. As a consequence, changes to precipitation had a different effect on annual fluxes. In the AN plot, peak N_2O fluxes tended to occur early in the experimental year, and changes in precipitation caused a small increase in N_2O fluxes, especially in the earlier, drier part of the year. Conversely peak N_2O fluxes in the Urea plot tended to occur later in the experimental year and changes in precipitation led to a slight decrease in N_2O fluxes. A similar pattern was observed with changes in soil pH at the Crichton experimental plot.

The sensitivity of N_2O to changes in N application rates was not expressly tested in this study because differences in N application rate across the sites were accompanied by variations in fertilizer type. By applying the model across all experimental plots, modelled estimates of annual N_2O emissions showed a simple linear increase in the rate of annual N_2O emissions for each fertilizer type. For example in both the Gleadthorpe experimental sites where each plot was managed with an increasing N target application rate, modelled emissions showed a perfect correlation ($R^2 = 1$) with the amount of N applied. This has also been well described in other studies (Gottschalk *et al* 2007, Hastings *et al* 2010), so in this study we focused on the sensitivity of the model to environmental drivers.

(c) *Comparison between measured, modelled and Tier 1 emission calculations*

Prior to the development of Tier 2/3 methodologies it is important to understand if they can provide a more accurate and robust representation of annual emissions when compared with Tier 1 methods. Despite the limitations described above, across both cropland and grassland plots, emissions estimated by DDC (figures 1(a), (b)) tended to provide a better estimate of annual emission than Tier 1 values (figures 6(a), (b)) when compared with the corresponding measured values. This is primarily because Tier 1 calculations assume that the rate of N fertilizer applied is only driver of N emissions directly from the soil. Therefore, when coupled with the N exported from the system in crop residue, annual emissions as estimated by Tier 1 methods in the control plots were lower than measured values. This, however, ignores natural processes in the soil such as microbial activity and the role other management events such as cultivation and harvesting have on emissions. These can be seen in measurements from the control plot at each site, which tended to show N_2O emissions despite the absence of N application. In addition, the Tier 1 methodology assumes that a consistent fraction of the synthetic N fertilizer or organic amendments is always emitted despite a difference in the chemical composition of the fertilizer type. However, both measured and modelled estimates in this study and other experimental work (Dobbie and Smith 2003, Velthof *et al* 1997 Jones *et al* 2007) showed that despite the same quantity of N applied, different fertilizer types led to different annual emissions (table 4), although the effect of different N types was far greater in the grassland site than arable sites.

5. Concluding remarks

While data limitation and model processes can lead to uncertainty in our outputs in terms of overall performance, DDC performed well across a range of cropland and grassland sites, particularly for fertilized fields (as almost all are in the UK), indicating that it is robust for UK conditions.

The methodology employed also aimed to demonstrate the sensitivity of N_2O emissions to uncertainty in available soil and climate inputs. Testing the sensitivity of the model to soil and climate inputs is extremely important especially if DDC is to be used to produce national scale N_2O emissions, or even to test the suitability of different mitigation scenarios. The methodology here allowed us to capture a significant part of the sensitivity of annual N_2O emissions, and also the importance of soil and climate inputs in driving estimates of annual emissions. This is essential as sometimes on a national scale specific soil descriptors can be omitted from national databases. Section 5 detailed some specific examples in the processes within the DDC model process that can be sensitive to changes in inputs. Some trends are apparent; as the soil pH level decreases across the sites, DDC became increasingly sensitive to changes in pH as an input. This was also true for clay content were the lower the site clay content the more sensitive DDC to changes in its value, but less so for bulk density. The higher the initial site value of soil pH or clay content the more sensitive DDC is to changes in bulk density.

Overall the results show that modelling N_2O emissions on a field scale can be challenging and that modelled estimates are dependent on complex interaction of different soil and climate inputs. Since not all sites show the same pattern, we show that DDC responses to combinations of drivers are complex and nonlinear. Our results also suggest that to apply the model across larger areas such as the UK an accurate soil, climate and management database is required in order to pick up the spatial and temporal variation in N_2O emissions which can more difficult to predict than for carbon dioxide emissions. If these challenges can be overcome estimates of N2O emissions from biogeochemical models such as DDC can provide a robust and accurate representation of annual N_2O emissions when compared to Tier 1 estimates which do not account for these variations.

Acknowledgements

This work contributes to the UK Defra funded projects AC0116: InveN_2Ory, and AC0114: the Greenhouse Gas Platform.

References

Abdalla M, Jones M, Ambus P and Williams M 2010 Emissions of nitrous oxide from irish arable soils: effects of tillage and reduced N input *Nutrient Cycling Agroecosyst.* **86** 53–65

Bell M J, Jones E, Smith J, Smith P, Yeluripati J, Augustin J, Juszczak R, Olejnik J and Sommer M 2012 Simulation of soil nitrogen, nitrous oxide emissions and mitigation scenarios at 3 European cropland sites using the ECOSSE mode *Nutrient Cycling Agroecosyst.* **92** 161–81

Butterbach-Bahl K, Baggs E M, Dannenmann M, Kiese R and Zechmeister-Boltenstern S 2013 Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Phil. Trans. R. Soc. B* **368** 1621

Butterbach-Bahl K, Breuer L, Gasche R, Willibald G and Papen H 2002 Exchange of trace gases between soils and the atmosphere in Scots pine forest ecosystems of the northeastern German lowlands 1. Fluxes of N_2O, NO/NO_2 and CH_4 at forest sites with different N-deposition *Forest Ecol. Manage.* **167** 123–34

Chadwick D R, Cardenas L, Misselbrook T H, Smith K A, Rees R M, Watson C J, McGeough K L, Williams J R, Cloy J M and Dhanoa M S 2014 Optimizing chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments *Eur. J. Soil Sci.* **65** 295–307

Dampney P, Dyer D, Goodlass G and Chambers B 2006 *Report for DEFRA project* Crop responses to different N fertiliser materials

de Bruijn A M G, Butterbach-Bahl K, Blagodatsky S and Grote R 2009 Model evaluation of different mechanisms driving freeze-thaw N_2O emissions *Agric. Ecosyst. Environ.* **133** 196–207

Del Grosso S J, Ogle S M, Parton W J and Breidt F J 2010 Estimating uncertainty in N_2O emissions from U.S. cropland soils *Glob. Biogeochem. Cycles* **24** GB1009

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 variables *Glob. Change Biol.* **9** 204–18

Fitton N, Datta A, Smith K, Williams J R, Hastings A, Kuhnert M, Topp C F E and Smith P 2014 Assessing the sensitivity of modelled estimates of N_2O emissions and yield to input uncertainty at a UK cropland experimental site using the DailyDayCent model *Nutrient Cycling Agroecosyst.* **99** 119–33

Gottschalk P, Wattenbach M, Neftel A, Fuhrer J, Jone M, Lanigan L, Davis P, Campbell C, Soussana J F and Smith P 2007 The role of measurement uncertaintyies for the simulation of grassland net ecosystem exchange (NEE) in Europe *Agric. Ecosyst. Environ.* **121** 175–85

Hastings A F, Wattenbach M, Eugster W, Li C, Buchmann N and Smith P 2010 Uncertainty propagation in soil greenhouse gas emission models: an experiment using the DNDC model and at the Oensingen cropland site *Agric. Ecosyst. Environ.* **136** 97–110

IPCC 2006 *IPCC Guidelines for National Greenhouse Gas Inventories; Prepared by the National Greenhouse Gas Inventories Programme* (Japan: IPCC)

Jones S K, Rees R M, Skiba U M and Ball B C 2007 Influence of organic and mineral N fertiliser on N_2O fluxes from a temperate grassland *Agric. Ecosyst. Environ.* **121** 74–83

Kurganova I N and de Gerenyu V O L 2010 Effect of the temperature and moisture on the N_2O emission from some arable soils *Eurasian Soil Sci.* **43** 919–28

Ogle S M, Eve M D, Breidt F J and Paustian K 2003 Uncertainty in estimating land use and management impacts on soil organic carbon storage for US agroecosystems between 1982 and 1997 *Glob. Change Biol.* **9** 1521–42

Palosuo T *et al* 2011 Simulation of winter wheat yield and its variability in different climates of Europe: a comparison of eight crop growth models *Eur. J. Agron.* **35** 103–14

Parton W J, Hartman M D, Ojima D S and Schimel D S 1998 DAYCENT: Its land surface sub-model: description and testing *Glob. Plant Change* **19** 35–48

Reay D S, Davidson E A, Smith K A, Smith P, Melillo J M, Dentener F and Crutzen P J 2012 Global agriculture and nitrous oxide emissions *Nat. Clim. Change* **2** 410–6

Rötter R P *et al* 2012 Simulation of spring barley yield in different climatic zones of Northern and Central Europ: a comparison of nine crop models *Field Crops Res.* **133** 23–36

Röver M, Heinemeyer O and Kaiser E A 1998 Microbial induced nitrous oxide emissions from an arable soil during winter *Soil Biol. Biochem.* **30** 1859–65

Saggar D L, Giltrap C, Li K and Tate R 2007 Modelling nitrous oxide emissions from grazed grasslands in New Zealand *Agric. Ecosyst. Environ.* **119** 205–16

Sansoulet J, Pattey E, Krobel R, Grant B, Smith W, Jego G, Desjardins R L, Tremblay N and Tremblay G 2014 Comparing the performance of the STICS, DNDC, and DayCent models for predicting N uptake and biomass of spring wheat in Eastern Canada *Field Crops Res.* **156** 135–50

Smith J and Smith P 2007 *Environmental Modelling: An Introduction* (Oxford: Oxford University Press) pp 1–178

Smith K A, Dobbie K E, Thorman R, Watson C J, Chadwick D R, Yamulki S and Ball C 2011 The effect of N fertiliser forms on nitrous oxide emissions from UK arable land and grassland *Nutrient Cycling Agroecosyst.* **93** 127–49

Smith P *et al* 1997 A comparison of the performance of nine soil organic matter models using seven long-term experimental datasets *Geoderma* **81** 153–225

Smith P, Powlson D S, Smith J U, Falloon P and Coleman K 2000 Meeting the UK's climate change commitments: options for carbon mitigation on agricultural land *Soil Use Manage.* **16** 1–11

Stocker T F, Qin D, Plattner G K, Tignor M, Allen S K, Boschung J, Nauels A, Xia Y, Bex V and Midgley P M 2013 Climate change 2013: the physical science basis *Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge: Cambridge University Press) pp 1–1535

Syakila A, Kroeze C and Slomp C P 2010 Neglecting sinks for N_2O at the Earth's surface: does it matter? *J. Itegrative Environ. Sci.* **7** 79–87

Teepe R, Brume R and Beese F 2001 Nitorus oxide emissions from soil during freezing and thawing periods *Soil Biol. Biochem.* **33** 1269–75

Velthof G L, Oenema O, Postma R and Beusichem M L 1997 Effects of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland *Nutrient Cycling Agroecosyst.* **46** 257–67

Vose D 2000 *Risk Analysis: A Quantitative Guide* (New York: Wiley)