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Quantifying annual N_2O emission fluxes from grazed grassland under a range of inorganic fertiliser nitrogen inputs

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ABSTRACT

The objective of the present study was to measure emissions of N_2O from fertilized grazed grassland that can be used to add valuable information to the limited existing data on N_2O fluxes from grazed grassland and aid the development of new country-specific EFs for direct emissions from soils in the UK. This was done by evaluating the effect on N_2O emissions of inorganic fertiliser N applied to grazed grassland soils over the range of N inputs 0–350 kg ha^{-1}. Nitrous oxide fluxes were measured using closed static chambers at 3 sites in England and Wales over a two-year period. Cumulative fluxes were calculated and the total emission regressed against applied inorganic fertiliser N in order to estimate the emission factor for N_2O emissions from soils. The data showed that, the emission factor for N_2O from inorganic fertiliser applied to grazed grassland soils in the UK differs from the IPCC default value of 1.25%. A nonlinear response of N_2O emissions to fertiliser N application rates was observed. Annual emissions of N_2O were estimated from a modelled function fitted to the measured data and after subtraction of the background flux resulted in emissions of 0.5 and 3.9 kg N_2O–N ha^{-1} yr^{-1} for an application of 100 kg N for three locations in the UK, one in the East and the other two in the West of the UK (after combining the data from two sites), respectively.

1. Introduction

The UK is required under the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC) to reduce its Greenhouse Gas (GHG) emissions by 12.5% relative to 1990 levels by 2008–2012 (United Nations, 1998; Jackson et al., 2009). The UK has also National commitments to meet a 34% cut in GHG emissions on 1990 levels by 2020 (DEFRA, 2009). Agriculture represents ca. 7% of all GHG emissions in the UK (2007) and was responsible in 2007 for 73% of the total nitrous oxide (N_2O) emissions and 37% of methane (CH_4) emissions (Jackson et al., 2009). The current UK GHG inventory predominantly uses the standard Tier 1 methodology of the Intergovernmental Panel on Climate Change (IPCC), which is generalised and simplified due to restricted data availability. In the case of N_2O, the UK methodology involves applying IPCC default emission factors (EFs) to UK activity data. In the case of emissions from soils, the EF used is 1.25% (IPCC, 1997) of the nitrogen (N) input (after volatilised N is subtracted in the case of fertiliser application) regardless of source of N location, climate and soil type.

Data from the literature shows that there is a large variability in the EFs for annual measurements of N_2O across the UK for both arable (Burford et al., 1981; Harrison et al., 1995; Smith et al., 1998a,b) and grassland (Ryden, 1983; Clayton et al., 1997; Dobbie and Smith, 2003) sites. Much of the data, especially for grassland ecosystems, has been collected from field sites in Scotland (Clayton et al., 1997; Smith et al., 1998b; Dobbie and Smith, 2003) and from only a few sites in the rest of the UK (Burford et al., 1981; Ryden, 1981; Harrison et al., 1995; Dobbie and Smith, 2003). Most of the existing data are from cut grassland and only a small number of data sets have been collected from grazed grassland. The presence of livestock in grazed grassland is expected to influence emissions due to the returns of N and C in excreta especially when added to the effect of the application of inorganic fertiliser and the impact of treading on the physical properties of the soil (Ball et al., 1999; Oenema et al., 1997).

The field measurements of biogenic gas emissions comprise a series of methodologies including chambers (closed and open),

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eddy covariance and long path methodologies (Mosier, 1989; Rochette and Eriksen-Hamel, 2008). The chamber technique is the most widely used methodology because it is relatively easy to use. However, use of this technique can be criticised due to limited spatial and temporal coverage, and intensity of labour. The challenge is to measure from sufficient sampling points to obtain a representative coverage of the spatial variability and to measure at a time in the day when the flux represents a daily mean. The temporal sampling strategy is also important in generating a representative annual flux: it is important to sample enough times throughout the year and at the right times to be able to obtain an accurate cumulative flux. Folorunso and Rolston (1984) estimated that 350 measurements were required in a 3 m × 36 m plot that was kept free of vegetation but received manure to estimate the "true" mean N_2O flux within ±10% of the estimated mean. They used 1.35 l chambers (each covering an area of 123 cm^2) for their measurements and found that soil parameters were spatially dependent but not the N_2O fluxes. They concluded that the use of larger chambers could decrease the number of observations required.

The objective of the present study was to measure emissions of N_2O from three grazed grassland sites within England and Wales, over a period of two years. These measurements would add valuable information to the limited existing data on N_2O fluxes from grazed grassland and aid the development of new country-specific EFs for direct emissions from soils in the UK.

The study examined the net effect of fertiliser applications on N_2O emissions from grazed grassland, without separating the contributions from fertiliser and from grazing.

2. Materials and methods

2.1. Sampling sites

Three sampling sites located in England and Wales with contrasting soil types and climatic regimes were selected to assess emissions of N_2O from grazed grassland. The field sites were Rowden, located at IGER North Wyke in Devon, England (now North Wyke Research at 50:46:10N and 3:54:05W), Cae Banadl at IGER Aberystwyth in Wales (now IBERS at 52:26:01N and 4:01:02W) and High Mowthorpe at ADAS in North Yorkshire, England (at 54:06:29N, 0:40:12W). Table 1 describes the locations and characteristics of the sites and soils under study. The soil at Rowden was of the Halstow series (Findlay et al., 1984), a brownish clay loam and characterised by being waterlogged for considerable periods of the year. The soil at Cae Banadl was on sloping land with good drainage. The soil at Cae Banadl has been mapped as a fine loam of the Denbigh series on the slope and Rheidol series at the foot of the slope (Rudeforth, 1970). This lower plot tended to be slightly wetter after rain but this was probably due to its position at the foot of the slope and being more poached because of a higher stocking rate. The soils at High Mowthorpe were of the Andover series, which are characteristically shallow, stony, free draining, with silty clay loam over chalk (Cope, 1976). The study was carried out over 2 years, from April 2006 to March 2008. The sward at Rowden was permanent grassland (>5 years old) and had not received any N fertiliser for more than 5 years. The Cae Banadl site had also been under ryegrass for >5 years and had received regular applications of NPK fertiliser. The site used at High Mowthorpe in the first year (Pony Paddocks), was permanent pasture, which had last been re-seeded over 15 years before the experiment was carried out and had received no mineral N fertiliser applied for at least 5 years. In the second year, the High Mowthorpe experimental site was moved to a new location (Blacksmiths Shop) which had been under permanent pasture for at least 10 years.

Each site was split into 4 paddocks of an equal size ranging from 0.2 to 1 ha. Ammonium nitrate (NH_4NO_3) fertiliser was applied to unreplicated paddocks using a Llely Superbowl fertiliser spinner at the Rowden site and a Fiona seed-drill adapted to provide a uniform distribution of granules at Cae Banadl and a Fiona Model G85 at the High Mowthorpe sites, to produce a response curve to increasing fertiliser application at a target application rate of either, 0, 75, 175 or 350 kg N ha^{-1} (treatments 0N, 75N, 175N and 350N). Fertiliser applications were split according to typical agronomic practice (Defra, 2000) (see Table 2). The 350N treatment at the Rowden site in the second year only received 310 kg N ha^{-1} (310N) due to atypically wet ground conditions making it unsuitable for fertiliser spreading with farm-scale field equipment (indeed the June and July applications were delayed by one month due to exceptionally high rainfall in summer 2007, so the last application of 40 kg N ha^{-1} could not be applied).

Phosphorus and potassium fertilisers were applied as necessary at agronomic rates from RB209 (Defra, 2000) following soil analyses for nutrient indices. The paddocks were rotationally grazed by young dairy or beef cattle between April and October. The cattle were allowed to graze the herbage down to a predefined sward height. They were then removed and the herbage allowed to regrow before reintroducing the cattle. Grass growth was assessed by regular compressed sward height determinations within each paddock using a rising plate meter (Castle, 1976). Grazing was

Table 1
Site locations and soil characteristics (pre-fertiliser applications). Values in parentheses correspond to the standard deviation for 3 samples.

Site	pH	Olsen P ($mg\,l^{-1}$)	K ($mg\,l^{-1}$)	Mg ($mg\,l^{-1}$)	Bulk density ($g\,cm^3$)	NO_3^-–N[a] ($kg\,N\,ha^{-1}$)	NH_4^+–N[a], ($kg\,N\,ha^{-1}$	Total N (%)	Total C (%)	Texture	Total rainfall ($mm\,yr^{-1}$)
Rowden, Yr 1	5.8 (0.1)	28.1 (1.4)	424.5 (4.3)	ND	1.0	0.055 (0.052)	6.82 (0.40)	0.65	6.7	CL	1036
Rowden, Yr 2	5.8 (0.1)	7.8–15.1[b]	248.6-294.9 [b]	104.0–152.5 [b]	ND	ND	ND	0.57–0.61 [b]	5.3–5.7 [b]	CL	1180
High Mowthorpe, Yr 1[c]	7.4	24	199	61	0.90	ND	ND	0.5	4.2	SCL over chalk	877
High Mowthorpe, Yr 2[c]	6.7	10.5	40.5	73	1.09	ND	ND	0.5	4.5	SCL over chalk	836
Cae Banadl, Yr 1	6.43 (0.02)	34.0 (0.4)	236.8 (4.0)	ND	0.93	10.99 (0.24)	1.85 (0.18)	ND	ND	LFL	1163
Cae Banadl, Yr 2	6.43 (0.02)	ND	ND	ND	ND	ND	ND	ND	ND	LFL	1274

Textures are: CL = clay loam; SCL over chalk = Silty clay loam over chalk; LFL = Loam-fine loam.
[a] Mean of all paddocks at 0–30 cm depth.
[b] Values for the second year are different for the different plots (after fertilisation in the first year) so ranges are reported, at 0–30 cm depth.
[c] Note that sites for High Mowthorpe changed between years 1 and 2.

Table 2
Management of the paddocks during years 1 and 2 at the 3 sampling sites. Fertiliser dates are given for all sites and the rates applied.

Site/treatment	Year 1, Rates of fertiliser application (kg N ha^{-1})						Total rate (kg N ha^{-1} yr^{-1})	Year 2, Rates of fertiliser application (kg N ha^{-1})						Total rate (kg N ha^{-1} yr^{-1})
Rowden	**19/4/6**	**10/5/6**	**30/5/6**	**20/6/6**	**11/7/6**	**1/8/6**		**27/3/7**	**24/4/7**	**22/5/7**	**31/7/7**	**29/8/7**		
0N	0	0	0	0	0	0	0	0	0	0	0	0		0
75N	40	0	35			0	75	0	40	35	0	0		75
175N	60	50	35	30		0	175	60	50	35	30	0		175
350N	80	70	60	50	50	40	350	80	70	60	50	50		310
High Mowthorpe	**27/4/6**	**02/6/6**	**19/6/6**	**24/7/6**	**22/8/6**			**26/3/7**	**17/4/7**	**15/5/7**	**18/6/7**	**17/7/7**	**10/8/7**	
0N	0	0	0	0	0	0	0	0	0	0	0	0	0	0
75N	50	0	25	0	0	75	76	0	42	33	0	0	0	75
175N	75	33	37	30	0	175	176	64	48	34	29	0	0	175
350N	101	50	68	71	60		350	83	68	58	51	50	40	350
Cae Banadl	**26/4/6**	**22/5/6**	**13/6/6**	**5/7/6**	**1/8/6**	**30/8/6**		**23/3/7**	**2/5/7**	**29/5/7**	**20/6/7**	**18/7/7**	**15/8/7**	
0N	0	0	0	0	0	0	0	0	0	0	0	0	0	0
75N	40	0	35	0	0	0	75	0	41	34	0	0	0	75
175N	58	50	36	31	0	0	175	60	50	35	30	0	0	175
350N	80	70	60	50	46	44	350	82	68	60	50	50	40	350

suspended when this value fell below 7.5 cm. The Rowden plots were grazed between 10/5/06 to 12/11/06 and 27/4/07 to 11/10/07; at Cae Banadl between 11/5/06 to 19/10/06, 26/4/07 to 19/10/07; and at High Mowthorpe between 30/04/06 to 18/09/06 and 04/05/07 to 10/10/07. Cattle numbers were adjusted on the basis of the quantity of herbage available on each plot during each grazing period. The resulting stocking density was between 2.6 and 5.1 LSU/ha for Rowden for both years; 1.2–2.7 LSU/ha in 2006 and 1.4–4.3 in 2007 for Cae Banadl and 13.3–18.2 LSU/ha in 2006 and 5.9–15.7 LSU/ha in 2007 for High Mowthorpe. At the Rowden site, once the cattle had been removed at the end of the year sheep were used to graze the remaining sward, which is normal grazing management in this part of the UK. The plots at Cae Banadl were also grazed by sheep in January of both years.

2.2. Gas sampling

A sampling protocol was developed similar to that by Rochette and Eriksen-Hamel (2008) and based on existing knowledge of the dynamics of N_2O fluxes following inorganic N fertiliser applications (see below).

The closed static chamber technique (Mosier, 1989; Jones et al., 2005) was used for collecting gas samples. At Rowden and High Mowthorpe, ten white PVC, not vented chambers (40 cm × 40 cm × 25 cm high, 5 mm thick wall; Dobbie et al., 1999) were placed in a diagonal transect in each paddock before collecting gas samples. The chambers were inserted to a depth of up to 5 cm to ensure an airtight seal. The volume enclosed by the chamber was approximately 32.0 l. The chambers were removed when cattle were present and when applying fertiliser but reinstated in the same positions when sampling. At the time of sampling the lids were placed on top of the chambers and a seal was achieved by a strip of adhesive Neoprene rubber foam 25 mm width × 5 mm thick or via a water filled groove on the chamber that the lid fitted in to. The chambers were generally put in place at least 2 h before sampling and the gas sampling was normally carried out between 10:00 and 14:00.

As in Rowden and High Mowthorpe, ten white PVC chambers per paddock were used at Cae Banadl at the start of the first year but all had a water filled groove. However, the plots at Cae Banadl were on a sloping site and this gradient, together with the stony nature of the soil made it difficult to insert the chambers to a sufficient depth to ensure an adequate seal, particularly when the soil was dry. A different design of sample chamber was therefore used at this site from November 2006 onwards. These chambers consisted of a metal frame that was permanently installed in the ground and a chamber that was positioned over this during the measurement period. These chambers enclosed a volume of 29.4 l. The chambers were kept in place by using 2 elastic bunjee cords hooked in small holes drilled in the metal frame. The seal was achieved between the frame and the chambers by a strip of the same Neoprene used in the other chambers. Sampling commenced immediately after securing the chambers to the metal frames and gas sampling was usually carried out between 10:00 and 14:00. This is normally the time of the day considered to be representative of the daily mean (Velthof and Oenema, 1995). Mosier (1989) recommended sampling at mean daily temperature when fluxes are low and variability is small.

Atmospheric samples were collected at the start and the end (five at each time) of the sampling run to provide background values for N_2O. These also represented the time zero N_2O samples (T0). Chamber lids were then placed on the chambers sequentially across the paddocks and after 40 min a gas sample was collected from each closed chamber (T40) via a sampling port fixed in the lid. The N_2O flux was calculated based on the linear increase in N_2O concentration inside the chamber from T0 (ambient) to T40 (Smith and Dobbie, 2001). Linearity checks were carried out routinely to ensure the values reported corresponded to the real flux (i.e. that the T40 measurement is within the linear part of the accumulation of gas inside the chamber) at Rowden and Cae Banadl. A previous study at High Mowthorpe but an earlier study carried out at the same location and with the same chambers demonstrated that emissions were linear in a similar sampling period on grassland following application of N fertiliser (DEFRA, 2006 *pers. comm.*).

The linearity checks in the present study were carried out by taking four gas samples from one of the chambers in each paddock at T0, T20, T40 and T60 min on every sampling occasion. A 50-ml syringe was used to collect the gas samples from the chambers which were then placed in pre-evacuated 20–22 ml headspace vials using a hypodermic needle. The glass vials had a chloro butyl rubber septum (Chromacol). The pre-evacuation was carried out using a vacuum pump. Sampling was carried out up to 50 times at each site throughout the year. At least a total of 60 samples were collected at one time including the samples from the chambers, linearity checks and ambient. Certified gas standards (1–10 ppm, Air Products and BOC, UK) were sampled on the day the samples from the chambers were collected using a 50-ml syringe and flushed through pre-evacuated 20–22 ml headspace vials using a second needle to ensure vials were not over pressurised. At the High Mowthorpe sites, a 25 ml sub-sample of the 50 ml sample was injected into the vial and allowed to reach atmospheric pressure. The samples and standards were analysed as soon as possible after collection (within a week) by gas chromatography (GC). For the Rowden and Cae Banadl samples a Perkin Elmer Clarus 500 GC and TurboMatrix 110 auto headspace sampler with an electron capture detector (ECD) were used. The separation column employed was a Perkin Elmer EliteQ PLOT megabore capillary (30 m × 0.53 mm i.d.) which was operated at 35 °C. The ECD detector was set at 300 °C and the carrier gas was N_2. For the High Mowthorpe samples, an Ai 94 GC fitted with an ECD was used (Uson Ltd., Bury St Edmunds, UK) coupled to a headspace autosampler (Tekmar, 7000). The separation column employed was of type Porapak QS, stainless steel with mesh size 50–80. The separation column comprised of two columns, column one of 75 cm length and column two of 245 cm length, both were operated at 60 °C. The ECD detector was set at 350 °C and the carrier gas was N_2.

Before each gas sampling occasion during the 'grazing period' the cattle were temporarily removed from the paddocks to facilitate a safe environment for the researchers and cattle.

Following fertiliser application and at the onset of prill degradation, measurements were carried out on 3 consecutive days starting on the first day that the fertiliser was applied. After this intensive sampling period, the sampling was 'event-driven' until the next fertiliser application. During the grazing period samples were taken when daily rainfall exceeded 10 mm or every 10–14 days, whichever happened first. During the winter period (non-grazing), the gas sampling was event-driven (when daily rainfall was more than 10 mm) or every 14–21 days. This regime provided a total of at least 50 measurements in a year from each paddock. This sampling regime was established based on the knowledge of the temporal emissions of N_2O following fertiliser application (Smith and Dobbie, 2001) and the effect of rainfall on N_2O emissions. In between events the emissions are expected to be low, so measurements were still carried out but with less frequency. The IPCC Good Practice Guidance recommends measuring frequently after events and less frequently when emissions are close to background levels (IPCC, 2000)

2.3. Soil and meteorological data

Meteorological data were recorded at each sampling site or at the nearest meteorological station (rainfall and air temperature), which was within 2 km of the field site. The air temperature inside and outside the chamber was measured at each site and used to correct the concentrations of N_2O inside the chamber. At the start of the experiment and prior to the first fertiliser application or the onset of grazing, soil pH, extractable P, K and Mg concentrations, and total N and C levels were measured from within each paddock (0–7.5 cm sampling depth, see Table 1). Background soil mineral N was also measured at the start of the experiment (0–30 cm in 2006 and 0–30 and 30–60 cm sampling depths in 2007, Table 1).

Additionally, gravimetric soil moisture content was determined at a depth of 0–10 cm, across all paddocks every time gas samples were collected.

2.4. Data analysis

As the data analysis plays a fundamental role in the determination of accurate emissions (mean values must be calculated to best represent the data set), we carried out an extensive analysis of the field data.

The data were analysed at several levels:

(1) to assess the results of the linearity checks;
(2) to calculate daily fluxes from the mean of 10 chambers in each paddock;
(3) to calculate cumulative annual fluxes from the daily means for each paddock on each site;
(4) to assess differences between the yearly fluxes in all locations;
(5) to assess differences in fluxes between years in each location.

Linearity checks: the data from the linearity checks were analysed by fitting linear and quadratic functions on each chamber data set (four samples per chamber for each sampling date) and testing the significance of the quadratic terms. The R^2 of the linear data sets was also assessed by quantifying the data frequency over a range of 10 histogram groups (R^2 from 0 to 100). Finally the slopes of both, data up to 40 and 60 min, were assessed to quantify if there was a difference in the trend between sampling at those end-points.

Daily fluxes: The *W*-test (Genstat version 10) to check normality was applied to the 10 data values for each treatment and sampling occasion, to determine if data sets did not have a normal distribution. If the test indicated that the distribution was normal, the normal (arithmetic) mean of the 10 data values was used to generate the daily flux value. When the *W*-test indicated that the distribution was not normal, we assumed that the data were either log normal or had a grouping distribution with several clusters of data points. Although it has been reported that N_2O fluxes follow a log normal distribution (Folorunso and Rolston, 1984; Velthof and Oenema, 1995) our sample size was too small (10 points) to be able to confirm log normality. The kernel density estimator of the mean (Silverman, 1986; Thompson, 2006) was therefore used to show whether there were clusters of data. If clusters of data were shown (typically 2–3 clusters per plot), the mean of cluster means (non-hierarchical) of the clusters was reported as the representative mean of the 10 data values.

Annual fluxes: the cumulative fluxes were calculated as the area under the curve (or trapezoidal method, France and Thornly, 1984) by using Genstat (versions 10–11) for the means obtained by the two different methods: all data calculated as normal means; a combination of normal and mean of cluster means. Year 1 was considered to be between the date of the first fertiliser application and the last date before the first application of the second year for Rowden and Cae Banadl. Year 2 was from the date of the first application of the second year and the final sampling in March 2008. For the High Mowthorpe sites the year was 12 months as the site changed in the second year. The cumulative fluxes calculated using the normal means were compared to the results from using the combination of the mean of cluster means and normal mean (Table 3).

Differences between years and locations: these were assessed for each site and both years and for each year and the three sites, the cumulative N_2O flux data using the normal means, were assessed using Genstat for fitting exponential functions against the fertiliser application levels.

3. Results

3.1. Soil and meteorological data

At the Rowden and Cae Banadl sites, the soil analysis showed that the levels of mineral N increased at the end of year 1 (Table 1). At High Mowthorpe two different sites were used and soil was not assessed at the end of both years. The soils at Rowden and Cae Banadl had much larger initial mineral N compared to the two High Mowthorpe sites. No other major changes were observed.

The average daily air temperature at Rowden ranged between 3.3 and 18.3 °C in 2006, 6.2 and 14.9 °C in 2007; at Cae Banadl it ranged between 4.6 and 18.4 °C in 2006 and 6.3 and 15.2 °C in 2007 whilst at High Mowthorpe temperatures were between 3.2 and 18.3 °C in 2006 and between 3.4 and 15.1 °C in 2007.

3.2. Data analysis of N_2O fluxes

The linearity checks carried out on each sampling day up to 60 min (data not shown) produced an average, for both Rowden

Table 3
Comparison of cumulative fluxes in g N ha^{-1} y^{-1} for all treatments and sites for Years 1 and 2 by using the normal mean and a combination of a normal mean and mean of cluster means.

Site/treatment	Year 1		Year 2	
	Normal mean	Normal + mean of cluster means	Normal mean	Normal + mean of cluster means
Rowden 0N	1945	4230	1068	2578
Rowden 75N	4074	8209	4543	11,953
Rowden 175N	8529	13,490	7866	12,003
Rowden 350N	24,295	32,081	–	–
Rowden 310N	–	–	25,703	48,740
Cae Banadl 0N	957	1700	−149	466
Cae Banadl 75N	3029	5351	854	2089
Cae Banadl 175N	14,458	19,761	5824	13,145
Cae Banadl 350N	36,012	51,057	34,963	51,278
High Mowthorpe 0N	571	873	1244	4846
High Mowthorpe 75N	897	1297	880	1245
High Mowthorpe 175N	2039	2281	2597	4741
High Mowthorpe 350N	8105	8604	13,046	15,675

and Cae Banadl sites, of 85% of the data showing a linear response for all the treatments (data not shown) and 12% of the data that followed a quadratic function. The rest of the data (3%) resulted in negative R^2 due to zero slope (no flux). Samples from the chambers were taken at 40 min so the linear regressions were assessed at both times. The results of the assessment of the R^2 to 40 min compared to the R^2 at 60 min, showed that there was a small improvement in the linearity at 40 min ($P < 0.05$). These results agree with other studies of linearity on the headspace (De Klein et al., 2003; Folorunso and Rolston, 1984).

The results from the calculation of the daily means by using normal means were smaller than the means obtained when combining normal and mean of cluster means (Table 3). The differences were larger for Rowden and Cae Banadl, and smaller for High Mowthorpe. This suggests that there could be a difference in the spatial variability in N_2O fluxes between the site on the East of the UK compared to the two sites on the West of the country. It is possible that generally the data sets from High Mowthorpe were closer to normal distributions compared to the other two sites (resulting in less difference between normal and cluster means), possibly reflecting less variability in soil nutrients (inorganic N in particular) and moisture. Velthof et al. (1996a,b) suggested that high stocking rates could cause a 'unnatural' uniform distribution of mineralizable C in grazed grassland, decreasing spatial variability. High Mowthorpe had the largest stocking densities of all sites so this may have contributed to the smaller spatial variability on this site.

We found that the mean of cluster means seemed to be biased by large values when these were the minority in the data set (see Fig. 1). This, caused the much larger values of the means of cluster means when compared to the normal means, and, combined with published data where normal means were used (Dobbie and Smith, 2003) gave us enough evidence to use the normal means instead of the means of cluster mean values. We decided therefore, for the calculation of cumulative fluxes to use the normal means of the 10 chambers in the paddocks.

3.3. Fluxes of nitrous oxide

Temporal N_2O fluxes measured at each of the three sites are shown in Fig. 2a–c from the daily calculated normal means. Fig. 2a shows the results for the first year for the Rowden site where the application of inorganic fertiliser produced an increase in N_2O emissions in the 75N, 175N and 350N treatments. A similar increase was observed at all three sites, but the effect was different in each of the two years of measurements at each site. Mean daily fluxes ranged between: −4.0 and 559.8 g N ha^{-1} d^{-1} for Rowden, −3.2 and 1611.2 g N ha^{-1} d^{-1} for Cae Banadl and −7.4 and 309.4 g N ha^{-1} d^{-1} for the High Mowthorpe site in year 1. In year 2 fluxes ranged between −6.6 and 853.2 g N ha^{-1} d^{-1} for Rowden, −5.4 and 1280.6 g N ha^{-1} d^{-1} for Cae Banadl and −13.2 and 1137.8 g N ha^{-1} d^{-1} for the High Mowthorpe site. The largest fluxes were generally observed in Cae Banadl in the high N treatments. The three sites showed generally smaller fluxes in the summer of 2006 compared to 2007 (see Fig. 2b and c for Cae Banadl and the High Mowthorpe sites). The rainfall data (not shown) showed little rain in summer 2006 compared to 2007 in the months between June and September. This difference is also reflected in the soil moisture at the three sites (Fig. 3 shows the data for Rowden). The fluxes at Rowden (Fig. 2a) showed in addition to the response to fertiliser applications, a large increase in emissions in the autumn (October and November), long after the last fertiliser application but when the animals were still grazing.

The cumulative fluxes for the three sites derived from the normal means were plotted separately against fertiliser rate applied and nonlinear (exponential) functions were fitted by using Genstat (Fig. 4a–c). The results showed there is a lack of linearity in the response of N_2O flux from fertiliser application but the relationships were significant for both years ($P < 0.001$ for Rowden

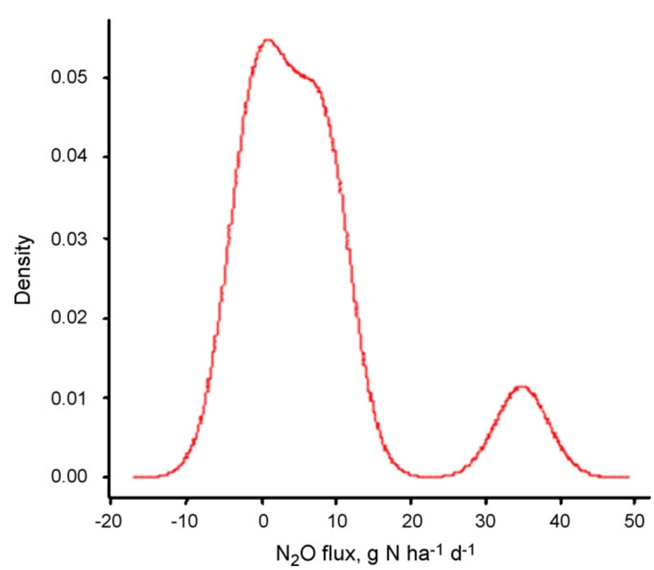

Fig. 1. Distribution of data set collected from 10 chambers in Rowden, 20/4/6 in the 0N paddock. Values were: 6.9, 9.8, 2.0, 34.8, 9.2, −2.8, 0.19, 0.90, −1.68, 6.8 g N_2O ha^{-1} d^{-1}. The normal mean was 6.6, the 2 group mean was 14.2 g N_2O ha^{-1} d^{-1}.

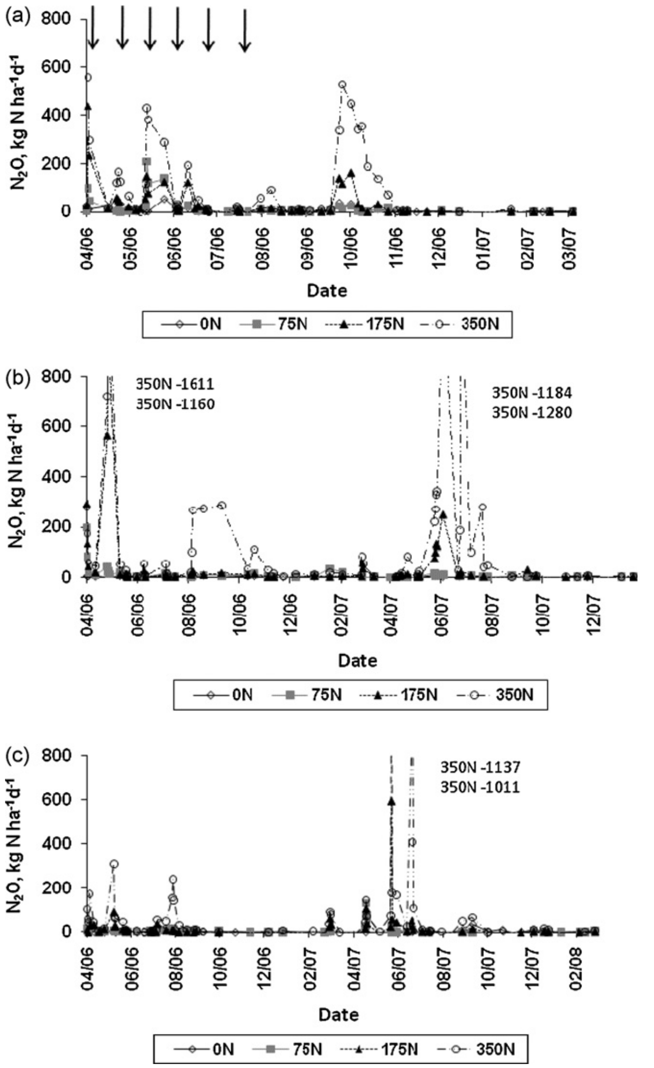

Fig. 2. Daily N_2O fluxes at: (a) Rowden for year 1; (b) Cae Banadl and (c) High Mowthorpe for years 1 and 2 (scales in vertical axes are the same but larger values are indicated in the boxes as treatment and flux in kg N ha^{-1} d^{-1}). See text for fertiliser dates and grazing periods. Arrows are the dates when fertiliser was applied. *X* axis is month/year.

and Cae Banadl and 0.002 for High Mowthorpe). The functions fitted were exponential:

$$Y = A + B * (R * *X)$$

where $R = e^{-k}$, k is the rate parameter, Y is N_2O flux in kg N_2O–N ha^{-1} yr^{-1}, X is fertiliser rate in kg N ha^{-1} yr^{-1} and $R^{**}X = R^X$.

The parameters of the exponential functions of N_2O fluxes vs fertiliser N applied for each of the three sites for both years are (see Table 4a showing the values and errors):

Rowden year 1: $Y = -2780 + 4720{*}1.0050^X$
Rowden year 2: $Y = -393 + 2110{*}1.00814^X$
Cae Banadl year 1: $Y = -19{,}460 + 19{,}450{*}1.00301^X$
Cae Banadl year 2: $Y = -1939 + 1584{*}1.00904^X$
High Mowthorpe site year 1: $Y = 70 + 474{*}1.00812^X$
High Mowthorpe site year 2: $Y = 711 + 250{*}1.01120^X$

These functions give values of N_2O emissions for a 100 kg N ha^{-1} yr^{-1} application of 5.0 and 4.4 kg N_2O–N ha^{-1} yr^{-1} for Rowden for years 1 and 2; 6.8 and 2.0 kg N_2O–N ha^{-1} yr^{-1} for Cae Banadl for both years 1 and 2; and 1.1 and 1.5 kg N_2O–N ha^{-1} yr^{-1} for the High Mowthorpe sites for years 1 and 2 (background values not subtracted). After subtracting the background the resulting fluxes are: 3.1 and

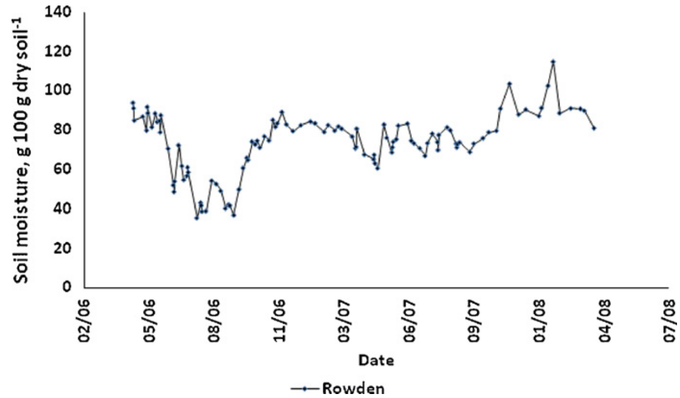

Fig. 3. Soil moisture at Rowden for years 1 and 2 (note that the value above 100% is due to the expression of moisture on dry soil weight basis). *X* axis is month/year.

2.6 kg N_2O–N ha^{-1} yr^{-1} for Rowden for years 1 and 2; 6.8 and 2.3 for Cae Banadl for both years 1 and 2; and 0.59 and 0.511 kg N_2O–N ha^{-1} yr^{-1} for the High Mowthorpe sites for years 1 and 2.

The comparison of the functions between years showed that for each site there was no difference between the A parameter ($P = 0.462$ for Rowden, 0.128 for Cae Banadl and 0.199 for the High Mowthorpe sites). The B parameter was not different for Cae Banadl ($P = 0.809$) but it was different for Rowden ($P = 0.025$) and the High Mowthorpe sites ($P = 0.005$) for both years. The *R* parameter was not different for Rowden ($P = 0.302$) in the two years and it was also not different for Cae Banadl ($P = 0.136$) and the High Mowthorpe sites ($P = 0.439$).

The responses of N_2O fluxes vs fertiliser N applied were also assessed between sites (see Fig. 5a and b). The regressions fitted through the data accounted overall for 98.5% of the variance for Year 1 and 99.4% for Year 2. This is the variance accounted for or the adjusted R^2 when comparing three sites and fitting the full model, i.e. separate parameters of the power or exponential function viz *A*, *B* and *R* in the function $y = A + B^*R^{**}X$. Table 4b shows the results of the statistical analysis using Genstat. For both years the results showed that the *A* parameters were not different for the 3 sites ($P = 0.096$ and 0.210 for years 1 and 2 respectively). The *B* parameter, showed significant difference between sites for each year ($P < 0.001$ for both years). The *R* parameter of the exponential function fitted to the results was not different for all sites and both years ($P = 0.591$ and 0.779 for years 1 and 2 respectively).

4. Discussion

The annual cumulative N_2O fluxes (calculated using the normal means of the 10 chambers in each paddock to estimate daily fluxes) were significantly related to the quantity of fertiliser N applied ($P < 0.001$ for Rowden and Cae Banadl, $P < 0.002$ for High Mowthorpe). The resulting N_2O fluxes from the functions obtained for an application of 100 kg N ha^{-1} yr^{-1}, for example, compare with values found in the literature for the UK for cut grassland (Dobbie et al., 1999) and grazed grassland (Smith et al., 1998b).

The relationships between fertiliser N input on cumulative N_2O found in this study was not linear, contrary to what has been reported in some studies (Dobbie et al., 1999) and as the IPCC EF indicates (IPCC, 1997).

Harrison et al. (1995) and Velthof et al. (1997) also found an increase of the percentage lost as N_2O when fertiliser N applied was increased. Fitting a power function through our data largely explained the variance for the two years of measurements and we found that there were some differences between sites and years. We found when comparing both years for each site that the B parameters were different for Rowden and Cae Banadl. When

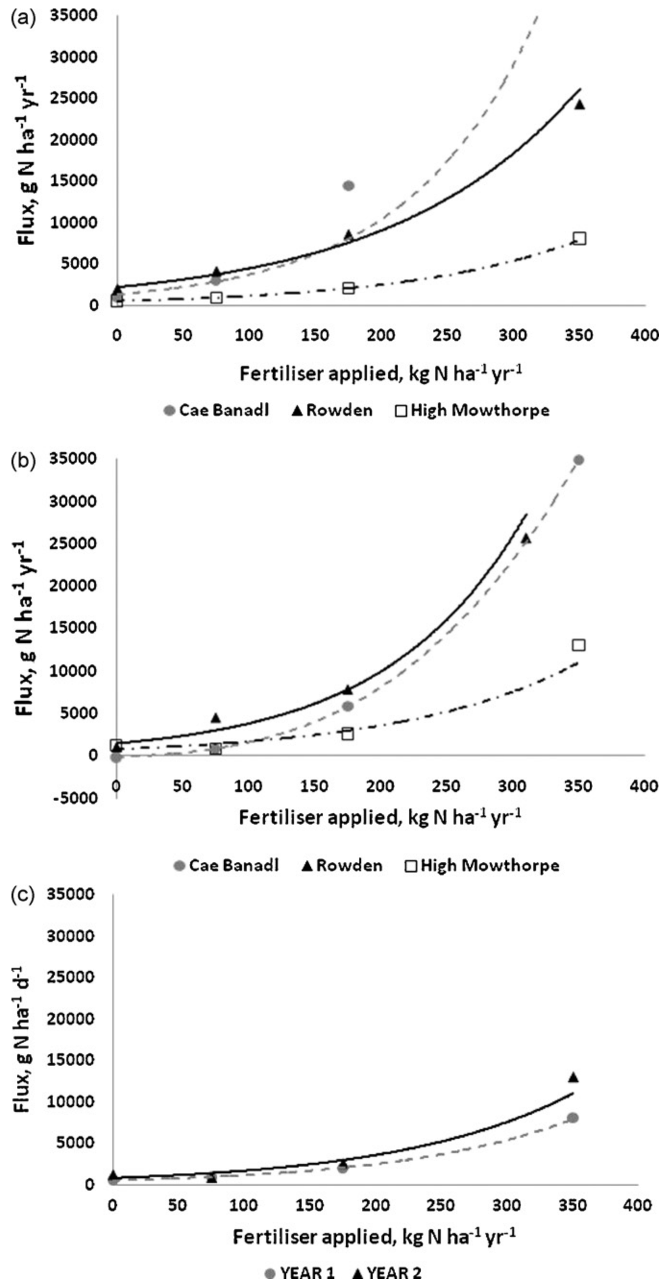

Fig. 4. Cumulative N_2O fluxes for years 1 and 2 for: (a) Rowden, (b) Cae Banadl, and (c) High Mowthorpe.

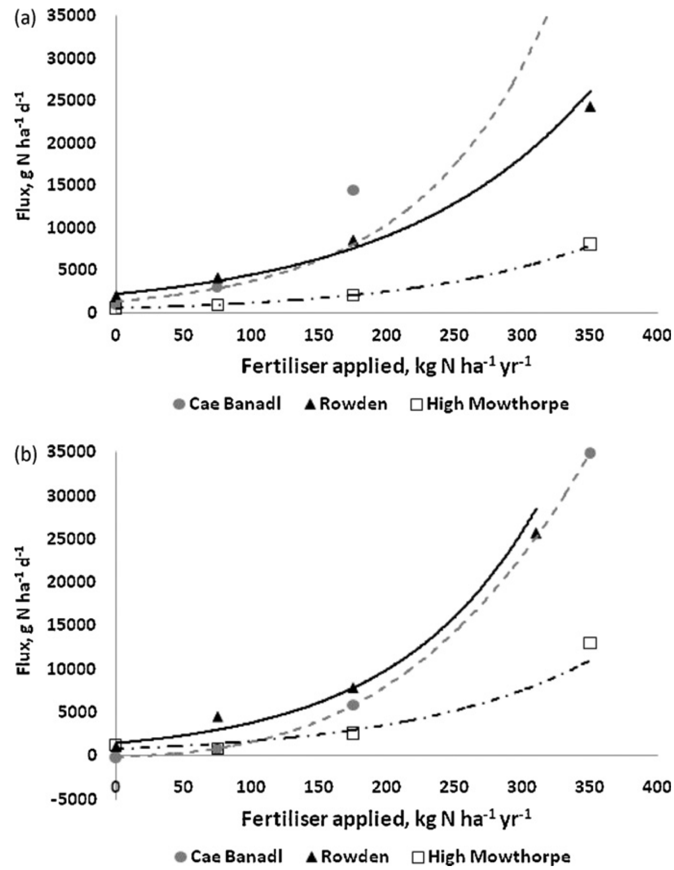

Fig. 5. Cumulative N_2O fluxes for the 3 sites on: (a) Year 1 and (b) Year 2.

comparing the three sites for the same year we found that the B parameters were different for both years. This suggests that the baseline emissions (when fertiliser added is zero) depend on the site which is probably the result of soil type combined with climate. The results from the *R* parameter however, showed that the shape of the response curves were similar at the various sites. Averaging over the three sites and two years of measurements however, is not straight forward, as mentioned earlier there are differences on the baseline emissions.

Due to the similarities in climate we compared the two sites located on the West of the UK (Rowden and Cae Banadl). We found when combining both data sets that there was a highly significant correlation between both sites and both years ($P < 0.001$). The intercepts and *R* parameters were the same, but the *B* parameter was slightly different. The variance explained by combining the data sets from these two sites was 93.1%. The resulting parameters and corresponding errors are summarised in Table 4c (error in brackets). The resulting equation for the fluxes obtained from fertiliser application is:

$$Y = -4330(4994) + 5062\ (5062) * [1.00564(0.00187) * *X]$$

The same analysis was carried out for both years for High Mowthorpe and the results showed that again the *B* parameter was

Table 4a

Comparison of the cumulative fluxes of N_2O between years within sites. Parameters of the fitted functions for the response of N_2O flux to fertiliser applied at each location over years 1 and 2 using normal means. Values in parentheses are the standard error of the parameter.

Site	Year	Parameters		
		A	*B*	*R*
Rowden	1	−2780 (3618)	4720 (2981)	1.00500 (0.00146)
	2	−393 (1897)	2110 (1234)	1.00814 (0.00170)
Cae Banadl	1	−19460 (15,972)	19450 (14,889)	1.00301 (0.00140)
	2	−1939 (2700)	1584 (1483)	1.00904 (0.00252)
High Mowthorpe	1	70 (672)	474 (412)	1.00812 (0.00229)
	2	711 (458)	250 (189)	1.01120 (0.00210)

Table 4b
Comparison of the cumulative fluxes of N_2O between sites within year. Parameters of the fitted functions for the response of N_2O flux to fertiliser applied for each year and three locations using normal means. Values in parentheses are the standard error of the parameter.

Site	Year 1			Year 2		
	A	*B*	*R*	*A*	*B*	*R*
Rowden	−2780 (5233)	4720 (4312)	1.00500 (0.00211)	−393 (1724)	2110 (1122)	1.00814 (0.00155)
Cae Banadl	−19460 (12863)	19450 (11990)	1.00301 (0.00112)	−1939 (1366)	1584 (751)	1.00904 (0.00128)
High Mowthorpe	70 (2500)	474 (1530)	1.00812 (0.00851)	711 (1069)	250 (443)	1.01120 (0.00491)

Table 4c
Final parameters for the fitted functions for the three sites and both years.

Site	Parameters		
	A	*B*	*R*
Rowden and Cae Banadl	−4330 (4994)	5062 (3901)	1.00564 (0.00187)
High Mowthorpe	439 (1617)	320 (795)	1.00992 (0.00678)

slightly different. Overall the variance if considering the same parameter *B* for both years was 87.5%, so the equation to calculate the fluxes from a location on the east of the UK is:

$$Y = 439(1617) + 320(795) * [1.00992(0.00678) * *X]$$

These equations would predict a flux of N_2O for a 100 kg N ha^{-1} yr^{-1} applied on the West of the UK of 4.6 kg N_2O–N ha^{-1} yr^{-1} and in the East of the UK of 1.3 kg N_2O–N ha^{-1} yr^{-1}. After removing the background (intercept or flux when $X = 0$) the emission for a 100 kg N ha^{-1} yr^{-1} application is 3.9 and 0.5 kg N_2O–N ha^{-1} yr^{-1} for the West and East of the UK, respectively. Values of fluxes reported for other countries in Europe for applications around 300 kg N ha^{-1} on grazed grassland were between 7 and 16 kg N_2O–N ha^{-1} yr^{-1} in The Netherlands (Velthof et al., 1996a,b). Using the above equations for the UK, the totals (after subtracting background) for a 300 kg N ha^{-1} yr^{-1} application are 22.3 and 5.9 kg N_2O–N ha^{-1} yr^{-1} in good agreement with the Netherlands values.

The value of N_2O flux for 100 kg N applied for the East of the UK is lower than the IPCC default value of 1.25% whilst the value for the West is much higher. One possible explanation for this is that the West of the UK is generally far wetter than the East of the UK. Results reported from studies in grazed grassland in Scotland showed values of emissions of up to 8 kg N_2O–N ha^{-1} yr^{-1} for 200 kg N ha^{-1} yr^{-1} application (Smith et al., 1998b) in agreement with the value for the West of the UK for the same application rate (10.5 kg N_2O–N ha^{-1} yr^{-1}, calculated from the equation for the West of the UK). Some of the studies carried out in Scotland where the weather is relatively wet (Dobbie and Smith, 2003; Smith et al., 1998b) have shown that fluxes are larger when the inorganic fertiliser used is ammonium nitrate (AN) compared to other types of fertilisers. These larger fluxes with AN however, do not always happen (Clayton et al., 1997). We suggest that the new EF's for the UK can be set according to regions, based on climatic conditions. Given similar N inputs at all sites, the higher rainfall and wetter soils in the west may have stimulated N_2O production 'hot-spots' to a greater extent generating larger and more frequent peak N_2O emissions as a result of intense denitrification resulting from anaerobic soil conditions.

The daily fluxes calculated using the normal means of the 10 chambers in each paddock demonstrated a significant effect of the application of inorganic fertiliser at all three sites and both years. Overall, the fluxes were larger in Rowden and Cae Banadl compared to the High Mowthorpe sites probably due to the larger annual rainfall at the former two sites (Table 2) producing higher soil moisture values. The results from the second year of measurements showed larger fluxes compared to the first year in all sites, most likely due to the higher soil moistures (see Rowden data in Fig. 3) due to higher rainfall (Table 2) at all sites.

Temperatures were generally slightly cooler in the second year although the minimum temperatures were generally greater. This is likely to have contributed to the larger fluxes in the second year. The daily fluxes at Cae Banadl reached much higher values than the other two sites (Fig. 2b), probably the result of the higher rainfall (see Table 1). Rowden showed a large flux two months after the last inorganic N fertiliser application in 2006 (Fig. 2a). These fluxes can be attributed to a relatively dry warm summer where there would have been an accumulation of N in the soil. The N_2O fluxes during this summer were very low as Fig. 2 shows possibly due to low microbial activity. Grazing was maintained during this period (when there was grass available) maintaining a regular recycling of N and C to the soil that underwent little processing. The arrival of the rain in the autumn would have reactivated the microorganisms, particularly in the warm temperatures, producing the large N_2O fluxes observed.

Several daily means resulted in negative values suggesting an N_2O sink. Net negatives fluxes have been observed before (Clayton et al., 1997) and may be due to highly wet conditions favouring consumption of atmospheric N_2O when no N is input to the soil (Clayton et al., 1997; Focht, 1978). The intercepts calculated from the equations above were 0.759 kg N_2O–N ha^{-1} yr^{-1} for High Mowthorpe and 0.732 kg N_2O–N ha^{-1} yr^{-1} for the combined Rowden and Cae Banadl and were similar to the value of 1 kg N_2O–N ha^{-1} yr^{-1} reported by Bouwman (1996).

The aim of this study was to determine the relationship between the rate of inorganic N application on N_2O emissions from grazed grassland. The emission factors that we have generated may have been more the result of the inorganic N fertiliser application (rather than from the combined effect of N application and urine deposition) since we could not be sure that urine was deposited within the chamber area. Other approaches are required to quantify N_2O emissions specifically from urine deposition (De Klein et al., 2003). However, there might be a case for producing an integrated emission factor for grazed grass in any improved inventory of greenhouse gases, i.e. to take account of both urine deposition and N fertiliser application, since the urine N content will reflect the inorganic N application rate and hence herbage N content. If we were to take this approach of developing an integrated emission factor, measurements with techniques such as eddy covariance (Hargreaves et al., 1996) or lysimeter scale (Moir et al., 2007) experiments would be appropriate.

5. Conclusions

Response curves of the emissions of N_2O from fertilised grazed grassland have been obtained for three locations in the UK. These curves provide emission factors for inorganic N fertiliser application rate under grazing. The response curves relating N_2O fluxes to fertiliser application were significant for all sites but not linear. The results of the comparison of the cumulative fluxes in all sites and both years suggested that a function might be derived based on similarities between sites for the West of the UK and another for the East with emissions of 3.9 and 0.5 kg N_2O–N ha^{-1} yr^{-1} after removing the background fluxes. However, further measurements would be required to take account of other factors influencing the response of fluxes to fertiliser application such as soil type. The data from this study add to the limited existing data on N_2O emissions on grazed grassland in the UK.

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References

Ball, B., Scott, A., Parker, J.P., 1999. Field N_2O, CO_2 and CH_4 fluxes in relation to tillage, compaction and soil quality in Scotland. Soil Till. Res. 53, 29–39.
Bouwman, A.F., 1996. Direct emissions of nitrous oxide form agricultural soils. Nutr. Cycl. Agroecosyst. 46, 53–70.
Burford, J.R., Dowdell, R.J., Crees, R., 1981. Emission of nitrous-oxide to the atmosphere from direct-drilled and ploughed clay soils. J. Sci. Food Agric. 32, 219–223.
Castle, M.E., 1976. A simple disc instrument for estimating herbage yield. J. Br. Grassland Soc. 31, 37–40.
Jackson, J., Choudrie, S., Thistlethwaite, G., Passant, N., Murrells, T., Watterson, J., Mobbs, D., Cardenas, L., Thomson, A., Leech, A., 2009. UK Greenhouse Gas Inventory, 1990 to 2007 Annual Report for Submission under the Framework Convention on Climate Change. AEA Technology.
Clayton, H., McTaggart, I.P., Parker, J., Swan, L., Smith, K.A., 1997. Nitrous oxide emissions from fertilised grassland: a 2-year study of the effects of N fertiliser form and environmental conditions. Biol. Fert. Soils 25, 252–260.
Cope, D.W., 1976. Soils in Wiltshire I: Sheet SU03 (Wilton). Soil Survey Rec. No. 32.
DEFRA, 2006. The behaviour of some different fertiliser-N materials: WP2 the effect of N fertiliser forms on nitrous oxide emissions. Final report to Defra, part of the NT26 programme. http://www.randd.defra.gov.uk/.
DEFRA, 2009. The UK Low Carbon Transition Plan. TSO (The Stationery Office).
De Klein, C.A.M., Barton, L., Sherlock, R., Li, Z., Littlejohn, R.P., 2003. Estimating a nitrous oxide emission factor for animal urine from some New Zealand pastoral soils. Aust. J. Soil Res. 41, 381–399.
Defra, 2000. Fertiliser Recommendations for Agricultural and Horticultural Crops (RB209), 7th edition. The Stationery Office, London.
Dobbie, K.E., McTaggart, I.P., Smith, K.A., 1999. Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. J. Geophys. Res. 104, 26891–26899.
Dobbie, K., Smith, K., 2003. Impact of different forms of fertilizer on N_2O emissions from intensive grassland. Nutr. Cycl. Agroecosyst. 67, 37–46.
Findlay, D.C., Colborne, G.J.N., Cope, D.W., Harrod, T.R., Hogan, D.V., Staines, S.J., 1984. Soils and Their Use in South West England. Bulletin no 14. Soil Survey of England and Wales, Harpenden.
Focht, D.D., 1978. Methods for analysis for denitrification in soils. In: Nielsen, D.R., Mac Donald, G.J. (Eds.), Nitrogen in the Environment, vol. 2. Academis Press, New York, pp. 433–490.
Folorunso, O.A., Rolston, D.E., 1984. Spatial variability of field-measured denitrification gas fluxes. Soil Sci. Soc. Am. J. 48, 1214–1219.
France, J., Thornly, J.H.M., 1984. Mathematical Models in Agriculture in Mathematical Models in Agriculture. Butterworths, London, UK, 335pp.
Harrison, R.M., Yamulki, S., Goulding, K.W.T., Webster, C.P., 1995. Effect of fertilizer application on NO and N_2O fluxes from agricultural fields. J. Geophys. Res. 100, 25923–25931.
Hargreaves, K.J., Wienhold, F.G., Klemedtsson, L., Arah, J.R.M., Beverland, I.J., Fowler, D., Galle, B., Griffith, D.W.T., Skiba, I.I., Smith, U., Welling, K.A., Harris, M.G.W., 1996. Measurement of nitrous oxide emission from agricultural land using micrometeorological methods. Atmos. Environ. 30, 1563–1571.
IPCC (Intergovernmental Panel on Climate Change), 1997. Greenhouse gas emissions from agricultural soils. In: Houghton, J.T., et al. (Eds.), Greenhouse Gas Inventory Reference Manual. Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories. IPCC/OECD/IES. UK Meteorological Office, Bracknell, UK.
IPCC, 2000. In: Penman, J., Kruger, D., Galbally, I., Hiraishi, T., Nyenzi, B., Emmanul, S., Buendia, L., Hoppaus, R., Martinsen, T., Meijer, J., Miwa, K., Tanabe, K. (Eds.), Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. IPCC.
Jones, S.K., Rees, R.M., Skiba, U.M., Ball, B.C., 2005. Greenhouse gas emissions from a managed grassland. Global and Planetary Change 47, 201–211.
Moir, J.L., Cameron, K.C., Di, H.J., 2007. Effects of the nitrification inhibitor dicyandiamide on soil mineral N, pasture yield, nutrient uptake and pasture quality in a grazed pasture system. Soil Use Manage. 23, 111–120.
Mosier, A.R., 1989. Chamber and isotope techniques. In: Andreae, M.O., Schimel, D.S. (Eds.), Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, Life Sciences Research Report 47. John Wiley, Chichester, pp. 175–187.
Oenema, O., Velthof, G.L., Yamulki, S., Jarvis, S.C., 1997. Nitrous oxide emissions from grazed grassland. Soil Use Manage. 13, 288–295.
Rochette, P., Eriksen-Hamel, N.S., 2008. Chamber measurements of soil nitrous oxide flux: are absolute values reliable? Soil Sci. Soc. Am. 72, 331–342.
Rudeforth, C.C., 1970. Soils of North Cardiganshire, Rothamsted. Soil Survey of England and Wales.
Ryden, J.C., 1981. N_2O exchange between a grassland soil and the atmosphere. Nature 292, 235–237.
Ryden, J.C., 1983. Denitrification loss from a grassland soil in the field receiving different rates of nitrogen as ammonium-nitrate. J. Soil Sci. 34, 355–365.
Silverman, B.W., 1986. Density Estimation for Statistics and Data Analysis. Chapman & Hall, London.
Smith, K.A., Dobbie, K.E., 2001. The impact of sampling frequency and sampling times on chamber-based measurements of N_2O emissions from fertilized soils. Global Change Biol. 7, 933–945.
Smith, K.A., McTaggart, I.P., Dobbie, K.E., Conen, F., 1998. Emissions of N_2O from Scottish agricultural soils, as a function of fertilizer N. Nutr. Cycl. Agroecosyst. 52, 123–130.
Smith, K.A., Thomson, P.E., Clayton, H., McTaggart, I.P., Conen, F., 1998. Effects of temperature, water content and nitrogen fertilisation on emissions of nitrous oxide by soils. Atmos. Environ. 32, 3301–3309.
Thompson, M., 2006. Representing data distributions with kernel density estimates. Amc technical brief. Analytical Methods Committee. Royal Soc. Chem..
United Nations, 1998. Kyoto protocol of the United Nations Convention of Climate Change. , In: http://unfccc.int/resource/docs/convkp/kpeng.pdf.
Velthof, G.L., Brader, A.B., Oenema, O., 1996. Seasonal variations in nitrous oxide losses from managed grasslands in The Netherlands. Plant Soil 181, 263–274.
Velthof, G.L., Jarvis, S.C., Stein, A., Allen, A.G., Oenema, O., 1996. Spatial variability of nitrous oxide fluxes in mown and grazed grasslands on a poorly drained clay soil. Soil Biol. Biochem. 28, 1215–1225.
Velthof, G.L., Oenema, O., 1995. Nitrous oxide fluxes from grassland in the Netherlands 1. Statistical analysis of flux-chamber measurements. Eur. J. Soil Sci. 46, 533–540.
Velthof, G.L., Oenema, O., Postma, R., Van Beusichem, M.L., 1997. Effects of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland. Nutr. Cycl. Agroecosyst. 46, 257–267.