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Nitrous Oxide Emission from Grazed Grassland Under Different Management Systems

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Abstract

Nitrous oxide (N_2O) emissions from grazed grasslands are estimated to be approximately 28% of global anthropogenic N_2O emissions. Estimating the N_2O flux from grassland soils is difficult because of its episodic nature. This study aimed to quantify the N_2O emissions, the annual N_2O flux and the emission factor (EF), and also to investigate the influence of environmental and soil variables controlling N_2O emissions from grazed grassland. Nitrous oxide emissions were measured using static chambers at eight different grasslands in the South of Ireland from September 2007 to August 2009. The instantaneous N_2O flux values ranged from -186 to 885.6 μg N_2O-N m^{-2} h^{-1} and the annual sum ranged from 2 ± 3.51 to 12.55 ± 2.83 kg N_2O-N ha^{-1} y^{-1} for managed sites. The emission factor ranged from 1.3 to 3.4%. The overall EF of 1.81% is about 69% higher than the Intergovernmental Panel on Climate Change (IPCC) default EF value of 1.25% which is currently used by the Irish Environmental Protection Agency (EPA) to estimate N_2O emission in Ireland. At an N applied of approximately 300 kg ha^{-1} y^{-1}, the N_2O emissions are approximately 5.0 kg N_2O-N ha^{-1} y^{-1}, whereas the N_2O emissions double to approximately 10 kg N ha^{-1} for an N applied of 400 kg N ha^{-1} y^{-1}. The sites with higher fluxes were associated with intensive N-input and frequent cattle grazing. The N_2O flux at 17°C was five times greater than that at 5°C. Similarly, the N_2O emissions increased with increasing water filled pore space (WFPS) with maximum N_2O emissions occurring at 60–80% WFPS. We conclude that N application below 300 kg ha^{-1} y^{-1} and restricted grazing on seasonally wet soils will reduce N_2O emissions.

Key words: nitrous oxide; grassland; emission factor; nitrogen input; soil temperature; water filled pore space; grazing frequency; soil type.

Introduction

The atmospheric concentration of the main greenhouse gases (GHG), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) has increased significantly since the pre-industrial era. Atmospheric N_2O concentration has increased from 270 ppb in 1750 to 319 ppb in 2005, and is estimated to account for approximately 6% of the predicted global warming (IPCC 2007). Additionally, N_2O contributes to ozone destruction because of its long life and high global warming potential which is 298 times that of CO_2 over a hundred-year period.

Worldwide, soils are considered to be the dominant source of N_2O, releasing an estimated 9.5 Tg

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N_2O-N y^{-1} (65% of global N_2O emissions), of which 3.5 Tg N_2O-N y^{-1} are estimated to originate from agricultural soils and 1 Tg N_2O-N y^{-1} from temperate grassland soils (IPCC 2001). Soil microbial activity produces N_2O emissions (Barton and others 2008), although recent work by Samarkin and others (2010) suggests the possibility of abiotic processes in N_2O formation in cold regions. Respiratory denitrification is considered the dominant source of soil N_2O emissions as anaerobic dentrifiers reduce nitrogen (N) oxides, for example, nitrate (NO_3^-), to nitric oxide (NO), to N_2O and finally to N gas (N_2). Soil N_2O emissions are also produced as a product of nitrification in which nitrifying microbes convert soil ammonium (NH_4^+) to NO_3^- under aerobic conditions (Barton and others 2008).

The net N_2O flux between the soil and the atmosphere is the result of the balance of production and consumption of N_2O within the near-surface soil. The availability of oxygen (O_2), carbon (C) and nitrogen (N) are important controls in the production of N_2O in soils. Apart from microbiological processes, the movement and fate of N_2O produced in the subsoil are mainly determined by the physical processes of molecular diffusion, convection, ebullition and entrapment, which further depend on soil temperature, soil moisture, rainfall amount, rainfall rate and other meteorological parameters (Clough and others 2005). The key driving variable for N_2O emissions from grassland in the summer months, once N fertilizer has been applied, is soil water content and its consequent effect on water filled pore space (WFPS) (Flechard and others 2007).

In Ireland, grasslands are predominantly used to provide feed for ruminants. As N is often limiting in grasslands, inorganic N fertilizers [for example, urea, calcium ammonium nitrate (CAN)] or organic N (farmyard manure or cattle slurry) are applied in significant amounts to maintain soil productivity. Fertilizer applications greater than the agronomic requirement result in surplus N which can be immobilized in the soil or lost through denitrification, leaching of NO_3, NH_4-N, and organic-N, volatilization through NO_x and NH_3, surface runoff and gaseous N_2O or NO emissions to the atmosphere.

Intensively managed grasslands are potentially a large source of N_2O in Ireland due to fertilizer N use and urine excretion by grazing animals combined with high rainfall, often exceeding 1200 mm y^{-1}. Uneven deposition of excretal N by grazing animals can result in 'hotspots' equivalent to an application of 400-2000 kg N ha^{-1} y^{-1} in the small affected area (Watson and Foy 2001), leading to wide spatial and magnitude variations in N_2O emissions.

The total land area of Ireland is 6.9 Mha of which 4 Mha are used for agriculture (Teagasc 2009). Therefore, 80% of agricultural land was devoted to silage, hay and pasture, 11% to rough grazing and 9% to crop production. Grasslands range from intensively fertilized pure grass swards to extensively managed grass–legume mixtures and semi-natural grasslands (FAO 2004).

Few, if any, direct measurements of nitrous oxide emissions from the Irish grassland sector are available (Hsieh and others 2005; Hyde and others 2006) and instead, the Irish Environmental Protection Agency (EPA) uses the default emission factor (EF) value of 1.25% (N fertilizer-induced N_2O) provided by the IPCC to quantify the flux (EPA 2009). Extrapolation of the IPCC default emission factor for Ireland as a region may not be appropriate due to differences in N fertilizer management (type, rate and application method), soil types, grazing regimes and regional climatic differences. Therefore, we set up an experiment to measure N_2O emissions and Emission Factors from grassland soils from sites across South West Ireland as a step towards calculating an improved national inventory of direct N_2O emissions from grassland soils. The objectives of this research were: (1) to acquire an unique 2-year data set and quantify the annual N_2O fluxes and N_2O emission factors; (2) to investigate the relationship between N_2O emissions and other meteorological parameters and (3) to examine the influence of N-input, soils and grazing frequency on N_2O fluxes.

Materials and Methods

Study Sites

In the spring of 2007, eight grasslands sites were selected in the South of Ireland (Figure 1). Nitrous oxide measurements were undertaken using the chamber technique (Skiba and others 1998) from September 2007 to August 2009. The period from September 2007 to August 2008 is hereafter referred to as year 1, and September 2008 to August 2009 as year 2. All sites are located at dairy farms. Three sites [Ballinhassig (BH), Carraig na bhFear (CF) and Donoughmore (D)] are privately owned whereas the other five sites [Clonakilty (CK), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)] are owned by Irish Government agricultural colleges and research farms. Five of the eight sites were intensively managed with stocking rates above 1.5 livestock units (LU) ha^{-1} (Teagasc 2009). All sites have control plots (free from fertilizer application and

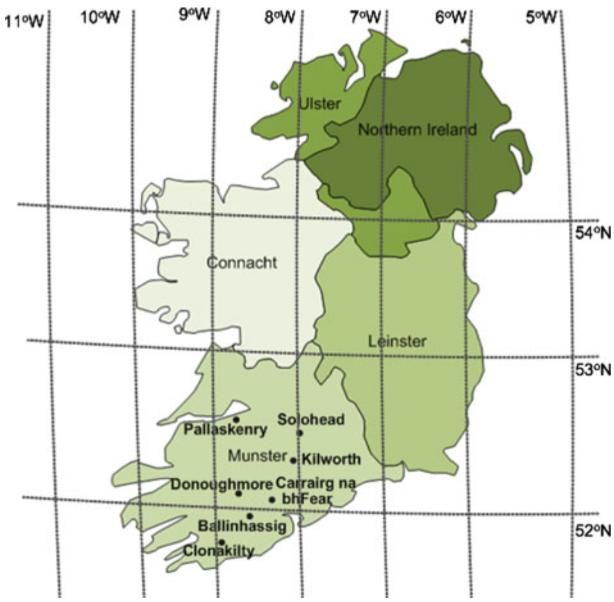

Figure 1. Location of the eight study sites in Munster, Ireland. Solohead1 (SH1) and Solohead2 (SH2) are located at the same farm.

grazing) for the measurement of background N_2O emissions. The sites were selected to represent the major soil types of Ireland, a range of dairy management practices and a range of meteorological conditions (for detail see Tables 1, 2, 3).

The Irish climate is temperate and humid with mean annual precipitation of approximately 1200 mm y^{-1} in the south west of the country. The average daily air temperature ranges from 5°C in winter to 15°C in summer. The site elevations ranged from 15 to 187 m above sea level. An overall description of the sites is given in Table 1. The soil characteristics are presented in Table 2. Most of the soils were loams with bulk density in the top 10 cm ranging from 0.88 to 1.05 g cm^{-3}. All sites were active pastures, regularly grazed and fertilized with inorganic and organic N fertilizers. The dominant grass species at all sites was perennial ryegrass (Lolium *perenne* L.). The Solohead1(SH1) site has clover and perennial ryegrass (PRG) (clover about 40–50% in July/August) and Donoughmore (D) has a very small fraction of clover (5–10% in July/August) (Table 3). The well-drained sites were podzols and the poorly drained sites were gleys (Table 2).

The management data (number of grazing animals, application of fertilizer and grazing events) for each site were collected regularly from farmers and farm managers. The management information is summarized in Tables 3 and 4. The organic N

Table 1. General Description of and Annual Average Soil Temperature and Total Annual Rainfall at the Eight Grassland Sites at which N_2O Emissions were Measured Between September 2007 and August 2009

Sites	County	Latitude	Longitude	Elevation (m)	Slope	Annual average soil temperature (°C)		Annual rainfall (mm)	
						Sep 07–Aug 08	Sep 08–Aug 09	Sep 07–Aug 08	Sep 08–Aug 09
Ballinhassig (BH)	Cork	51.47 °N	9.59 °W	79	Undulating (2–6°)	11.01	10.57	980.4	1060.48
Clonakilty (CK)	Cork	51.36 °N	10.17 °W	69	Rolling (7–12°)	12.29	11.03	1001	1050.48
Donoughmore (D)	Cork	51.58 °N	10.12 °W	187	Flat (0–1°)	10.16	9.65	1500.29	1580.1
Carriag nab h Fear (CF)	Cork	51.58 °N	9.55 °W	104	Undulating (2–6°)	10.85	8.50	1220.93	1350.39
Pallaskenry (PK)	Limerick	51.44 °N	10.17 °W	15	Undulating (2–6°)	10.98	10.34	1040.74	1040.62
Kilworth (KW)	Cork	51.37 °N	9.40 °W	51	Undulating (2–6°)	10.98	10.47	960.1	1100.2
Slohead1 (SH1)	Tipperary	51.35 °N	9.43 °W	102	Undulating (2–6°)	10.15	10.27	1370.36	1320.6
Solohead2 (SH2)	Tipperary	51.35 °N	9.38 °W	98	Flat (0–1°)				

Annual average temperature and annual rain is the same for SH1 and SH2.

Table 2. Soil Physical and Chemical Characteristics in the 0–10 cm Horizon of the Eight Grassland Sites Measured in July 2007 at which N_2O Emissions were Measured Between September 2007 and August 2009

Sites	Soil type	Bulk density (g/cm^3)	Sand %	Silt %	Clay %	Porosity %	C%	N%	C/N	pH	Organic matter %	NO_3-N (mg/g)	NH_4-N (mg/g)
BH	Grey brown podzolic	1.02 ± 0.04	33.03 ± 1.44	38.16 ± 1.45	28.80 ± 0.01	62 ± 2.43	3.42 ± 0.20	0.39 ± 0.03	8.76 ± 9.66	5.8 ± 0.1	7.24 ± 0.55	3.7 ± 0.4	50 ± 2.04
CK	Brown podzolic	0.99 ± 0.06	52.81 ± 2.22	27.93 ± 1.48	19.26 ± 0.30	63 ± 3.81	4.77 ± 0.13	0.57 ± 0.01	8.30 ± 3.24	5.9 ± 0.3	9.22 ± 0.25	74.05 ± 3.2	35.4 ± 0.28
D	Gley	1.00 ± 0.13	44.62 ± 1.30	43.50 ± 0.18	11.87 ± 1.48	63 ± 8.19	4.54 ± 0.05	0.35 ± 0.01	12.97 ± 3.06	6.7 ± 0.0	8.45 ± 0.16	5.3 ± 0.6	46.1 ± 1.06
CF	Brown podzolic	0.88 ± 0.08	39.22 ± 0.84	37.72 ± 0.52	23.05 ± 0.31	68 ± 6.18	5.67 ± 0.39	0.64 ± 0.04	8.85 ± 9.28	6.4 ± 0.0	9.9 ± 0.38	36.1 ± 2.3	60.35 ± 0.91
PK	Grey brown podzolic	1.03 ± 0.10	49.5 ± 0.25	31.5 ± 1.61	19 ± 1.36	61 ± 5.92	4.84 ± 0.02	0.56 ± 0.05	8.64 ± 8.93	5.4 ± 0.1	9.62 ± 0.04	22.9 ± 0.3	53.05 ± 0.77
KW	Brown podzolic	1.08 ± 0.07	52.68 ± 1.38	25.50 ± 2.91	17.81 ± 1.52	59 ± 3.82	4.17 ± 0.19	0.49 ± 0.02	8.51 ± 6.11	5.7 ± 0.1	7.87 ± 0.06	23.2 ± 1.0	19.65 ± 0.77
SH1	Gley	0.99 ± 0.14	45.85 ± 1.32	31.90 ± 2.90	22.25 ± 1.57	63 ± 8.90	4.73 ± 0.13	0.57 ± 0.01	8.29 ± 3.26	6.3 ± 0.0	8.48 ± 0.07	30.6 ± 0.6	14.55 ± 0.21
SH2	Gley	0.83 ± 0.09	18.98 ± 0.73	41.67 ± 1.28	39.35 ± 1.95	69 ± 7.48	7.82 ± 0.25	0.97 ± 0.04	8.06 ± 5.21	6.5 ± 0.0	14.77 ± 0.31	11.45 ± 2.1	30.6 ± 0.28

± *Shows standard deviations of the mean values.*

Table 3. Management Type, Stocking Rate (LU ha^{-1}), Animal Type, Inorganic and Organic N-input and Total N-input at Eight Grassland Sites [Ballinhassig (BH), Clonakilty (CK), Donoughmore (D), Carraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)] at which N_2O Emissions were Measured Between September 2007 and August 2009

Sites	Grassland management types	Species composition	Live Stock Unit (LU) ha^{-1}	Ruminant types	Inorganic N (kg N ha^{-1} y^{-1})		Fertilizer type	Organic N (kg N ha^{-1} y^{-1})		Cattle grazing N (kg N ha^{-1} y^{-1})		Total N (kg N ha^{-1} y^{-1})	
					Sep 2007–Aug 2008	Sep 2008–Aug 2009		Sep 2007–Aug 2008	Sep 2008–Aug 2009	Sep 2007–Aug 2008	Sep 2008–Aug 2009	Sep 2007–Aug 2008	Sep 2008–Aug 2009
BH	Extensive	Ryegrass	1.0	Dairy cow/ Sheep	100.41	100.41	CAN	NA	40.17	53.2	91.39	153.4	232
CK	Intensive	Ryegrass	2.50	Dairy cow	124.83	124.83	Urea/CAN	77.59	46.55	175.07	260.77	377.49	432.15
D	Intensive	Ryegrass/ Clover	3.0	Dairy cow	347.97	244.2	Urea/CAN/ Pasteur Sward	NA	160.09	56.76	42.33	404.73	446.62
CF	Intensive	Ryegrass	1.80	Dairy cow	169.05	202.86	CAN	53.46	48.6	150.22	166.03	372.7	417.5
PK	Intensive	Ryegrass	1.80	Dairy cow	188.51	173.0	Urea/CAN/ Sweet Grass	NA	NA	152.58	115.15	341.09	288.15
KW	Intensive	Ryegrass	2.47	Dairy cow	169.29	141.5	Urea/CAN	NA	NA	186.61	193.4	355.9	334.9
SH1	Extensive	Ryegrass/ Clover	1.50	Dairy cow	NA	NA	NA	240.23	120	100.48	56.45	340.7	176.5
SH2	Extensive	Ryegrass	1.50	Dairy cow	39.74	52.95	Urea	NA	NA	81.25	87.6	121	140.6

CAN = calcium ammonium nitrate; NA = not applied.

applied was estimated from the number of grazing animals and the N excretion rate for Irish livestock (for example, for dairy cows 1 LU = 85 kg N) (Anon 2006). The site SH1 received three applications of slurry (organic N) and no inorganic fertilizer in the second year of this study (Table 3). The sites BH, PK and KW received no slurry. The sites CK, D, CF, PK and KW were grazed frequently, whereas BH, SH1 and SH2 were not frequently grazed (for details see Table 4).

Environmental Measurements

Meteorological stations were established at 7 of the 8 sites to measure rainfall, soil temperature and soil moisture: a single station was installed for SH1 and SH2 as both these sites were located within 1 km of each other. A tipping bucket rain gauge (Young Transverse MI 52203, USA) was used to measure rainfall with a resolution of 0.1 mm. A soil temperature probe (Campbell Scientific, UK) and soil moisture TDR probe (Campbell Scientific, UK) at a depth of 5 cm were installed at the seven locations. Soil temperature, soil moisture and rainfall were logged at half hour intervals on a CR 200 data logger (Campbell Scientific, UK). The WFPS was determined as a ratio of volumetric water content and soil porosity. Soil porosity was calculated as [1 − (bulk density/particle density)] × 100, using a particle density of 2.65 g cm^{-3} (Barton and others 2008).

Soil Analysis

The near-surface (0–10 cm) soil characteristics (bulk density (BD), organic matter (OM), C%, N%, NO_3-N, NH_4-N and pH) were measured in July 2007 (Table 2). Soil samples for BD were taken using bulk density rings (5 cm × 8 cm, Eijkenkamp Agrisearch Equipment BV, The Netherlands) at five points at each site: at the corners and at the center of the square plot (size 10 × 10 m).

All the soil samples were returned to the laboratory, dried at 50°C, physically crushed and sieved through a 2-mm aperture sieve. To measure the BD, the smaller-than-2 mm portion of the soil sample was weighed and measured volumetrically by displacement. Bulk density was calculated as follows:

$$\mathrm{BD} = \frac{\text{dry weight} < 2\text{ mm soils}}{(\text{volume of ring} - \text{volume of} > 2\text{ mm soils})} \tag{1}$$

This equation for BD omits the volume and mass of particles larger than 2 mm, therefore removing the influence of stones. Particle size analyses (PSA) were undertaken using the pipette method in which particle sizes are inferred using Stokes Law of settling from the sedimentation time of dispersed soil particles.

Soil organic carbon (SOC) was analyzed using dry combustion methods on a CN elemental analyzer (Elementar, Vario Max CN, Hanau Germany). Organic matter content was estimated by loss on ignition (LOI). The dried and sieved soils were subsampled and dried for 24 h at 150°C. These dried samples were weighed to within 0.0001 g. The samples were then ashed at 360°C for 2 h in a computerized 'force air' (Blue M) ashing oven and re-weighed. Loss on ignition was calculated as follows:

$$\mathrm{LOI}\ (\%) = \frac{(\text{oven dry soil weight} - \text{ashed soil weight})}{\text{oven dry soil weight}} * 100 \tag{2}$$

Nitrate and NH_4^+ were determined by the colorimetric method with an auto analyzer (Quikchem 8000 FIA+, Lachat Instruments, Milwaukee, WI, USA).

Nitrous Oxide Flux Measurement Techniques

Nitrous oxide emissions were measured using the closed chamber technique (Skiba and others 1998). Each of the chambers was made of a cylinder of polyvinyl chloride (PVC) with a volume of 0.28 m^3 (height = 45 cm; diameter = 28.2 cm). The chamber had an aluminium ring base inserted into the ground during sampling. Additionally, a vent tube (length = 10 cm) and thermocouple (ELE International, UK) for internal air temperature were also installed in each chamber. The vent tube was used to equalize the enclosed and ambient air pressure (Davidson and Savage 2002). The site sampling points [eight chamber points for managed (+N) sites and three chamber points for control (unmanaged) plots (0 N)] were fixed and located along two grid lines, 4-m apart (Dobbie and Smith 2003b). To maintain experimental consistency, the same sampling points were used throughout the sampling period. Control plots were established at each site to allow the background N_2O flux to be estimated. These control plots were free of management activates, for example, N-input, grazing and so on. These control plots were in a fenced area of the same field as the sampling plots. Data from the control plots were used to estimate the emissions factor (EF).

Table 4. Grazing Pattern (Animal Number, Grazing Days) at Eight Grassland Sites [Ballinhassig (BH), Clonakilty (CK), Donoughmore (D), Carraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)] at which N_2O Emissions were Measured Between September 2007 and August 2009

Month	Year	BH		CK		D		CF		PK		KW		SH1		SH2	
		GD	AN	GD	AN	GD	AN	GD	AN	GD	AN	GD	AN	GD	AN	GD	AN
Sep	1st	25–30	15	17	95	10	51	23	60	20	155	26–30	5	16–18	27	–	–
	2nd			15	95	15	50	25	60	15	140	24–30	5	–	–	09–10	18
Oct	1st	01–15	15	–	–	15	51	22	60	18	155	01–03	5	24–26	27	04–07	27
	2nd	–	–	–	–	10	50	20	60	10	140	–	–	08–11	18	09–10	18
Nov	1st	–	–	–	–	20	51	25	60	10	148	07–11	4	–	–	07–08	27
	2nd	–	–	–	–	18	50	22	60	15	150	09–14	5	29–30	18	28	18
Dec	1st	–	–	–	–	25	51	27	60	–	–	–	–	–	–	–	–
	2nd	–	–	–	–	20	50	19	60	–	–	–	–	–	–	–	–
Jan	1st	–	–	21	50	02	51	25	60	–	–	–	–	–	–	–	–
	2nd	–	–	13	70	21	50	20	60	–	–	–	–	–	–	–	–
Feb	1st	–	–	11	75	25	51	28	60	–	–	–	–	–	–	28–29	18
	2nd	–	–	05/26	80/102	20	50	23	60	–	–	–	–	–	–	–	–
Mar	1st	10–30*	20*	03/31	90/93	30	51	03	60	18	159	23–26	5	–	–	–	–
	2nd	–	–	19	120	25	50	20	60	13	150	24–28	5	14–15	18	01–02	18
Apr	1st	–	–	17	95	–	–	02	60	05	200	23–25	5	23–27	18	20	18
	2nd	15–30 20–30*	25 15*	08/30	140/160	19	50	24	60	10	190	22–25	5	–	–	–	–
May	1st	–	–	12	95	02	51	04	60	05/25	200/203	18–20	5	–	–	24–25	18
	2nd	01–05/15–31 17–30*	25/25 15*	21	170	21	50	22	60	20	190	13–18	5	–	–	01–02	18
Jun	1st	25–30	15	03/27	95/95	05	51	05	60	14	191	02–05/21–23	5/5	06–10	18	23	18
	2nd	01–05/10–20 15–25*	25/25 15*	18	170	17	50	26	60	18	180	–	–	–	–	21–23	18
Jul	1st	01–15	15	21	95	15	51	01	60	08/31	191/173	03–07/28–31	5/5	13–19	18	20–21	18
	2nd	01–07 07–30*	25 15*	09/30	170/170	25	50	24	60	20	190	25–27	5	19–21	18	–	–
Aug	1st	–	–	19	95	20	51	20	60	23	163	23–26	5	–	–	11	18
	2nd	–	–	20	170	–	–	23	60	20	160	25–31	5	19–20	18	03–04	18

GD = grazing date, AN = animal number on the day of grazing.
**Sheep and cattle grazing, 1st year = September 2007–August 2008, 2nd year = September 2008–August 2009.*

The rate of increase of the N_2O concentration in the headspace of the chamber gives a direct estimation of the N_2O flux between the soil and the atmosphere (Flechard and others 2007). Four gas samples, each of 12-ml volume were taken at 20-min intervals over 1 h. At each time interval the chamber inner temperature was also recorded. The measurements were carried out weekly from March to November and monthly from December to February. The soil temperature and soil moisture were recorded at a depth of 5 cm on each measurement occasion using a hand held digital thermometer (Hanna, THV-240-020 W, UK) and soil moisture metre (Delta-T Devices, HH2, UK). These soil moisture data were used to determine the WFPS.

The N_2O concentration in each sample was analysed using a gas chromatograph (GC 3800, Varian, USA) fitted with packed column (Porapak QS 80-100 MESH, Sigma Aldrich, USA) using an electron capture detector at 300°C. This system was attached to a Combi Pal automatic sampler (CTC analytics, Switzerland) which extracted a sample of 750 µl from the sampling vial and injected it into the GC. Gases of known N_2O concentrations were used as reference points for the chromatography system. The analysis time of each sample was approximately 9 min. The areas under the N_2O peaks were integrated using a Star chromatography work station version 6.2 (Varian, USA) to find the N_2O concentration (Hyde 2004).

Hourly N_2O emissions (µg N_2O-N m^{-2} h^{-1}) were estimated from the slope of the linear increase in N_2O concentration during the chamber lid closure period (Holland and others 1999). The daily N_2O flux at each site was estimated using the arithmetic mean of the fluxes from the individual chambers (Dobbie and Smith 2003b; Barton and others 2008). Annual emission rates were estimated by integrating hourly rates with time (Flechard and others 2007). The annual emission factors for N_2O were estimated using

$$\mathrm{EF} = \frac{\mathrm{N_2O - N,\ total\ (+N) - N_2O - N,\ total(0N)}}{\mathrm{Total\ \text{-}\ N\ (applied)}} \tag{3}$$

where EF is the emission factor (N_2O-N emitted as % of N applied), and N_2O-N total (+N) and N_2O-N total (0N) are the cumulative N_2O emissions (kg N_2O-N ha^{-1} y^{-1}) from managed (+N) and unmanaged (0N) plots, respectively. The total N applied (combined inorganic N, slurry N and N estimated from excreta of grazing animals) is the rate of N applied during the study (kg N ha^{-1} y^{-1}) (Barton and others 2008).

Statistical Analysis

The normality of the distribution of the data was analyzed using the Shapiro–Wilk normality test. The *T* test was used to evaluate the differences in N_2O emissions between managed (+N) and control (0N) sites; N_2O emissions from less frequently grazed and frequently grazed sites and N_2O emissions from different types of soils. When the standard assumptions of normality were violated, the Mann–Whitney Rank Sum test was used. Differences were considered significant at the *P* less than 0.001 level. All the calculations, statistical analysis and graphical outputs were determined using MATLAB (Math works USA, 7.6.0, R2008a).

Results

Meteorological Variables

The annual rainfall is shown in Table 1 and the monthly rainfall in Figure 2. The annual rainfall ranged from 960 to 1580 mm. The sites D, CF, PK and SH (SH1 and SH2) experienced greater rainfall than the other sites. Site D had the greatest amount of rain throughout the study period commensurate with its highest elevation (187 m). Year 2 had greater rainfall than year 1. The winter months received most rain and the summer months were also moist with summer monthly rainfall of approximately 50 mm at all sites.

The monthly average soil temperature (at 5 cm depth) over the 2 years is shown in Figure 3A and annual averages in Table 1. The monthly average soil temperature ranged from winter lows of 4.5°C to summer highs of 16.3°C. There was little variation between sites. As grass requires a minimum temperature above 6°C for growth, this suggests that there is grass growth for more than 9 months of each year (Frame 1992).

The monthly average WFPS (at 5 cm depth) over the 2 years is shown in Figure 3B. Over the summers the soil WFPS ranged from 30.3 to 85.2%, whereas over the winters the range was 49.1 to 99.5%. In general, SH1 and SH2 with their gley soils had higher soil moisture contents throughout the whole period compared to the other six sites.

Soil Characteristics

The soil characteristics are shown in Table 2. Bulk density (of top 10 cm) of the soils ranged from 0.83 to 1.03 g cm^{-3}, whereas the porosity ranged from 59 to 69%. From texture analysis the soils were classified as clay loam, sandy loam or medium loam. The C% in most of the sites ranged from 4.3

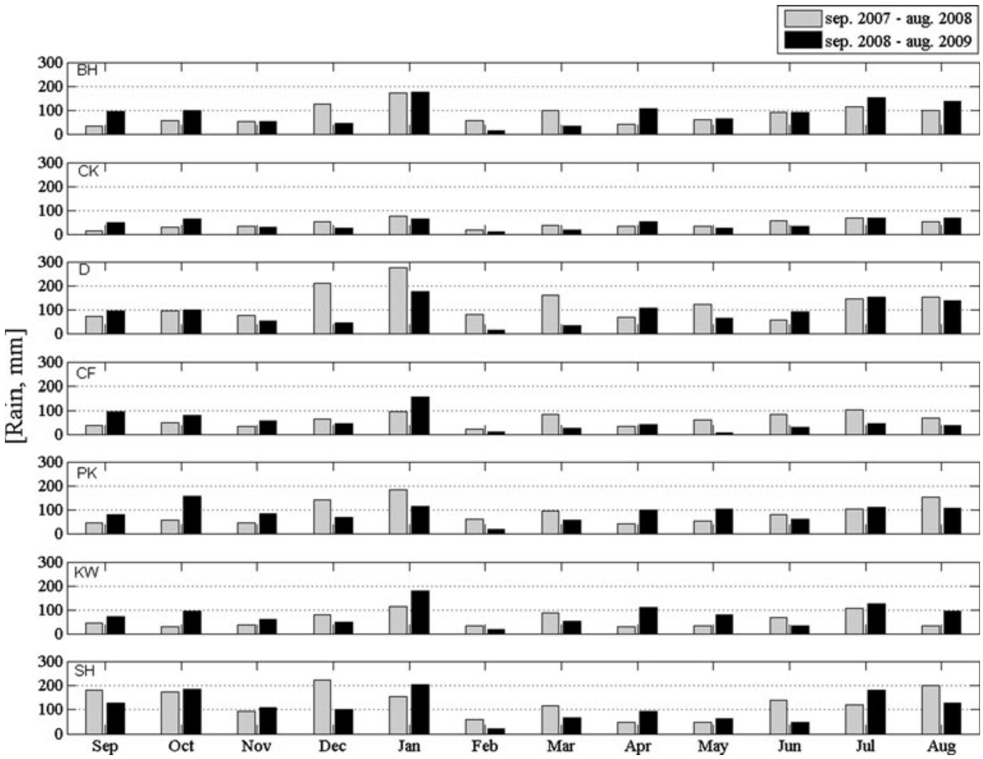

Figure 2. Monthly total rain (mm) from September 2007 to August 2009 at each of the eight study sites [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead]. Solohead1 and Solohead2 have the same data as both are located at the same farm.

to 5.4%, whereas SH2 had a C% of 7.2%. The OM% ranged from 7.2 to 14.7%. The N% ranged from 0.3 to 0.9 and the pH values ranged between 5.4 and 6.7. The C/N ratio was found to be in the range of 8.06 to 12.97. The NO_3-N and NH_4-N ranges were between 3.7 to 74.0 and 14.55 to 60.35 mg g^{-1}, respectively. The NO_3-N contents at CK site were higher than all other sites (for detail see Table 2).

N_2O Fluxes

The hourly N_2O fluxes from all sites [managed (+N) and unmanaged (0N)] from September 2007 to August 2009 are shown in Figure 4. The N_2O fluxes were episodic in nature with small pulses throughout the year and higher pulses in summer. The hourly emission ranged from 315 ± 57.4 to 885.6 ± 40 µg N_2O-N m^{-2} h^{-1} for the managed area (+N), whereas it ranged between 97 ± 1 and 334 ± 102.8 µg N_2O-N m^{-2} h^{-1} for control (0 N) plots. The highest hourly N_2O emissions greater than 500 µg N_2O-N m^{-2} h^{-1} were measured at CK, D, CF and PK in both the years. During the summers, elevated N_2O emissions coincided with elevated WFPS, high surface soil temperature and N application events. The highest peak emission was observed at CF on 4 July 2007, shortly after N fertilizer application when the soil temperature was 15°C and WFPS was 55%. The N_2O emissions from frequently grazed sites were consistently higher than those emissions from less frequently grazed sites.

The mean N_2O fluxes varied widely between most of the sites with maximum emission at CK. Across all sites, the mean N_2O flux ranged from 36.94 to 133.74 µg N_2O-N m^{-2} h^{-1} (Table 5). Occasional short-term negative peaks were also observed at all sites. The hourly uptakes ranged from −20 ± 22.2 to −186.6 3 ± 1 µg N_2O-N m^{-2} h^{-1} for managed (+N) and from −29 ± 20 to 159 ± 1 µg N_2O-N m^{-2} h^{-1} for control (0 N) area. The highest uptake rates were measured at CF, BH and SH1. The maximum N_2O uptake was observed at CF on 11 June 2009 when the soil was very dry with the soil temperature of 13°C and 38% WFPS. The N_2O fluxes from managed (+N) sites were found to be significantly higher than from control plots (0N) (*P* less than 0.001) as shown in Figure 4.

The estimated annual emissions for year 1 was in the range of 2 ± 3.51 to 11.6 ± 3.11 kg N_2O-N ha^{-1} y^{-1}, whereas for year 2 it ranged from 2.44 ± 1.98 to 12.55 ± 2.83 kg N_2O-N ha^{-1} y^{-1} for +N (Figure 5). The maximum value was observed at the CF site. Most of the sites, for example D, PK, KW, SH1 and SH2, had higher fluxes in year 1 than in year 2. From control sites (0N), the annual flux ranged between -1.59 ± 1.03

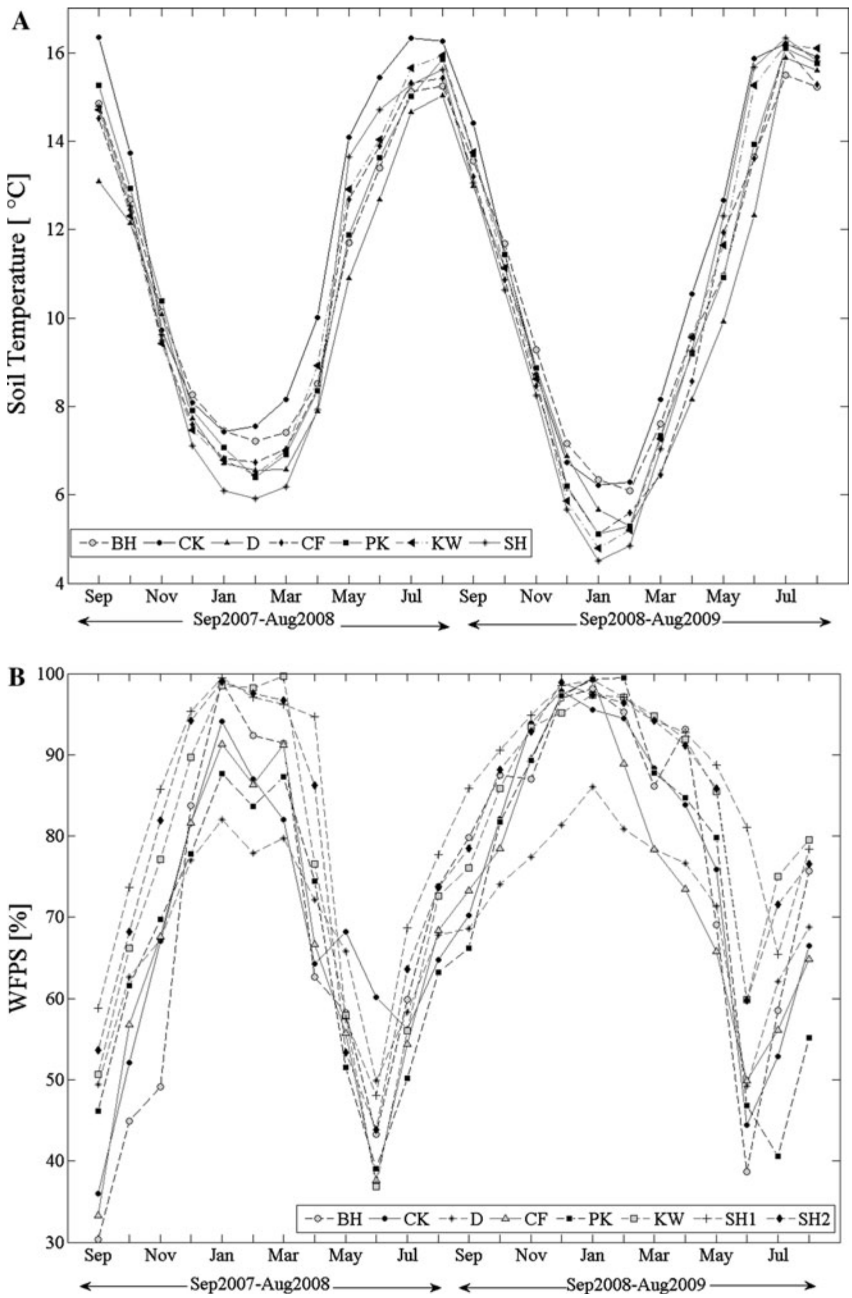

Figure 3. **A** Mean monthly soil temperature measured at 5 cm and **B** mean monthly soil WFPS% at 5 cm soil depth from September 2007 to August 2009 at each of the eight study sites [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)].

and 2.56 ± 1.43 kg N_2O-N ha^{-1} y^{-1} in year 1 and from 0.63 to 2.83 kg N_2O-N ha^{-1} y^{-1} in year 2. The annual N_2O fluxes along with their standard errors are given in Figure 5.

There was a substantial variation in the emissions factor (EF) which ranged from 1.14 to 3.07. Sites PK and CK gave the highest EF in both the years (Figure 6). The EF from CK, PK, KW and CF are higher than the IPCC default value of 1.25% whereas BH, D, SH1 and SH2 were similar to the IPCC value. The overall EF was 1.81% which is about 69% higher than 1.25%, the IPCC default EF.

Figure 7 shows the frequency distribution of measured fluxes which tended to be log normal after transforming the data set (due to negative fluxes). The bulk of the distribution was found in the range of 25–125 μg N_2O-N m^{-2} h^{-1}, which resulted in approximately 61% of the total fluxes.

The Relationship Between Annual N_2O Flux and Total N-Input

A non-linear exponential relationship was found between the annual N_2O fluxes and the total N-input at all sites (Eq. 4, Figure 8).

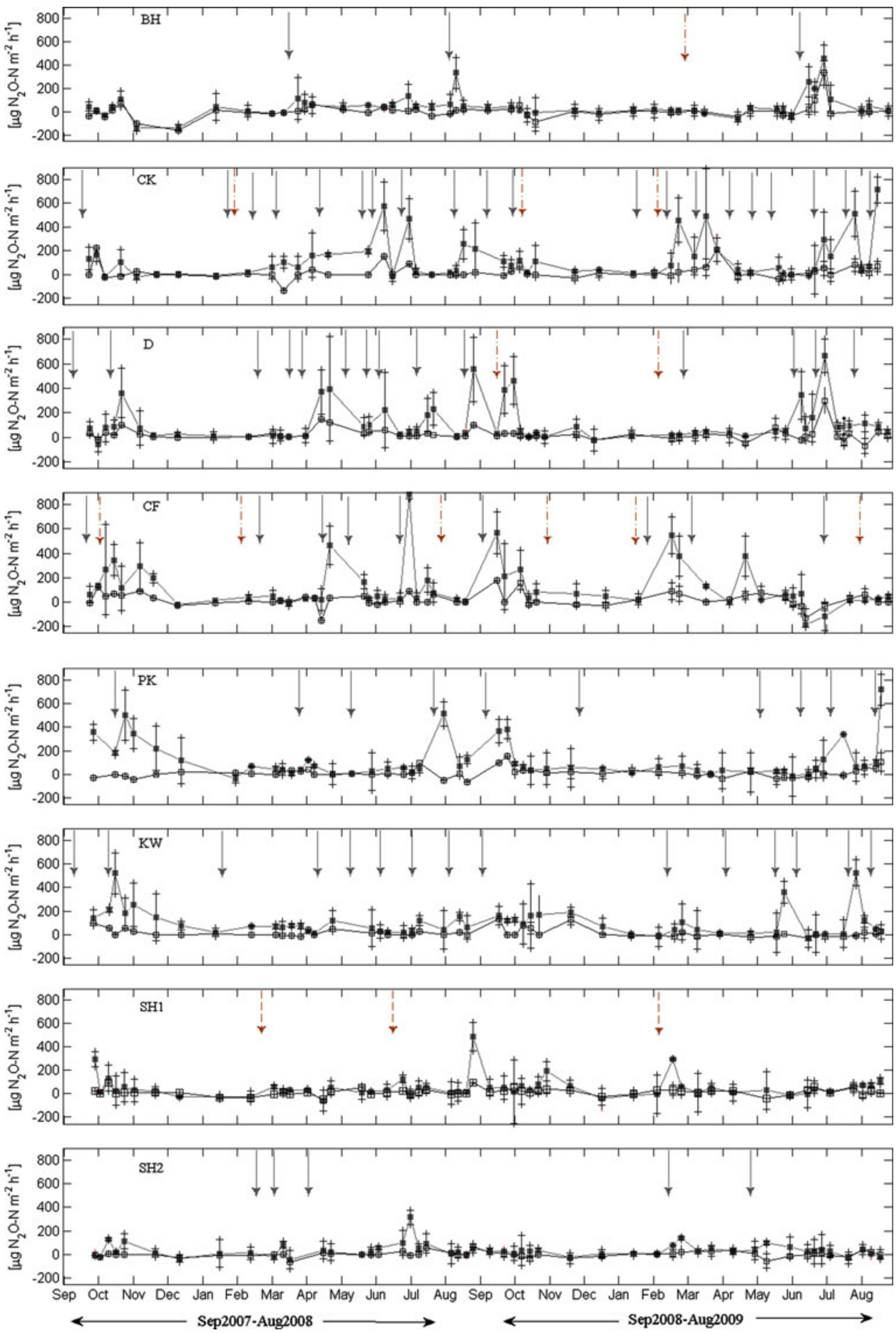

Figure 4. N_2O flux time series from September 2007 to August 2009 for Eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)]. (*Filled squares*) shows N_2O fluxes from treatment sites (+N) whereas (*empty squares*) shows N_2O fluxes from control sites (0N). *Solid arrows* indicate time of inorganic fertilizer application and *dotted arrows* indicate time of slurry application.

$$F = 1.33 \times e^{[0.004 \times \mathrm{N-Input}]} \qquad (4)$$

where F is the annual N_2O flux and N-input is the total N applied in the field. A linear relation was found to have an $R^2 = 0.62$, compared to the exponential relation with $R^2 = 0.77$. An exponential relationship has also been reported by Cardenas and others (2010), Kim and others (2010) and Eckard and others (2006).

Two different clusters of annual fluxes at two different ranges of total N-input were observed (Figure 8) which might suggest some threshold N-input above which the N_2O emissions increase exponentially. Therefore, the data from two other

Table 5. Instantaneous N_2O Flux and Mean Flux Description at Eight Grassland Sites [Ballinhassig (BH), Clonakilty (CK), Donoughmore (D), Carraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)] at which N_2O Emissions were Measured Between September 2007 and August 2009

Sites	Instantaneous flux (μg N_2O-N m^{-2} h^{-1})				Mean flux (μg N_2O-N m^{-2} h^{-1})
	Minimum (+N)	Minimum (0N)	Maximum (+N)	Maximum (0N)	
BH	−141 ± 28.8	−159 ± 1	456.6 ± 119.4	334 ± 102.8	44.94
CK	−20 ± 22.2	−31.8 ± 21	573 ± 204	225 ± 1	133.74
D	−54 ± 60.6	−70 ± 60	667.8 ± 135.4	150.6 ± 1	112.75
CF	−186.6 ± 1	−148 ± 1	885.6 ± 40	177 ± 1	126.67
PK	−34 ± 37.2	−67.2 ± 1	718.2 ± 129	152 ± 1	123.09
KW	−28.8 ± 74.4	−29 ± 20	519.6 ± 172	137 ± 1	104
SH1	−60.6 ± 87.6	−40.8 ± 30.4	489.6 ± 126.6	97 ± 1	53.36
SH2	−31.8 ± 28.2	−53.4 ± 61.8	315 ± 57.4	66.1 ± 1	36.94

0N = control plots with no fertilizer input; +N = managed site where N was applied through fertilizer, grazing and slurry.

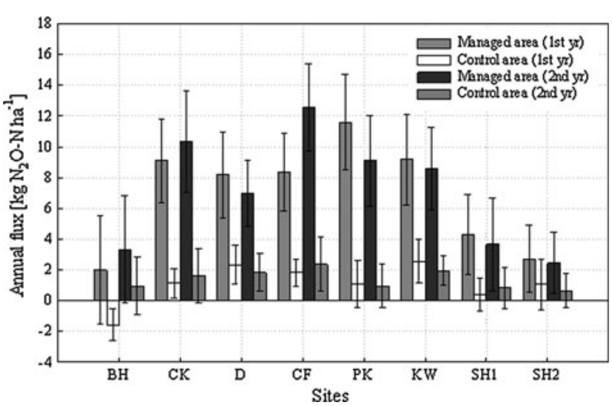

Figure 5. Annual N_2O fluxes (with ±standard error) across eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)]. 1st year is from September 2007 to August 2008, whereas 2nd year is from September 2008 to August 2009. Managed sites are those which received a continuous supply of N through inorganic fertilizers, slurry and animal grazing. Unmanaged sites were totally free from any management activity.

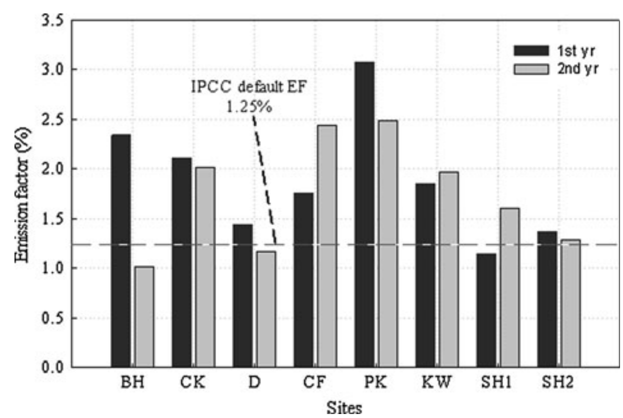

Figure 6. Emission factors across eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)]. 1st year is from Sep 2007 to Aug 2008, whereas 2nd year is from September 2008 to August 2009. The *horizontal line* shows the IPCC default EF value of 1.25%.

studies (Cardenas and others 2010; Kim and others 2010) were used to clarify the relationship between N_2O emissions and N-input. The results show a more exponential relationship between N applied and N_2O emissions with a less clear signature of threshold (Figure 8). However, at an N applied of below 300 kg N ha^{-1} y^{-1}, the N_2O emissions are approximately 5 kg N_2O-N, whereas the N_2O emissions double to approximately 10 kg N_2O-N ha^{-1} y^{-1} for an applied N of 400 kg N ha^{-1} y^{-1}.

The Relationship Between N_2O Fluxes and Soil Temperature

A sigmoidal curve was found to fit the binned mean daily temperature data with N_2O flux data from all the sites (Eq. 5, Figure 9) (Schmidt and others 2000).

$$F = \frac{110.18}{1 + e^{-\left[\frac{T_s - 6.90}{2.06}\right]}} \tag{5}$$

where F is the N_2O flux and T_s is the soil temperature.

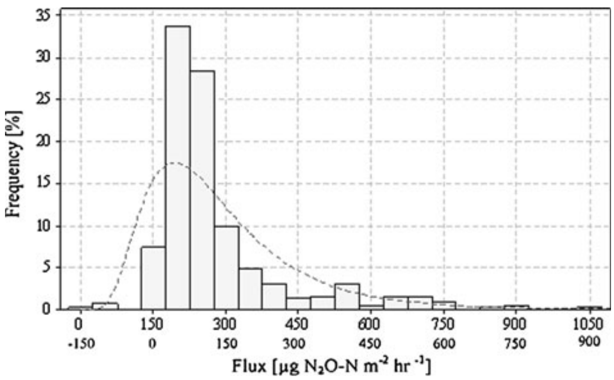

Figure 7. Frequency distribution of instantaneous N_2O fluxes across eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)]. *Upper horizontal axis* shows the transformed data, whereas *lower axis* shows original data.

A rapid increase of N_2O flux was noted once the temperature exceeded 5°C. The temperature range of 0 to 17°C showed an excellent agreement with N_2O flux ($R^2 = 0.83$). Beyond 17°C the N_2O flux remains constant.

The Relationship Between N_2O Fluxes and Water Filled Pore Spaces (WFPS%)

A Gaussian curve was found to fit the binned mean daily WFPS% against N_2O fluxes from all the sites (Eq. 6, Figure 10). A similar relationship was used by Schmidt and others (2000).

$$F = 146.10 \times e^{\left[-0.5\left(\frac{\mathrm{WFPS}-69.49}{16.98}\right)^2\right]} \quad (6)$$

where F is N_2O flux observed.

The maximum N_2O flux pulses were found to occur at WFPS between 60 and 80%, with peak emission at approximately 70% WFPS.

Grazing Frequency and N_2O Fluxes

The sites that were frequently grazed produced higher mean N_2O fluxes (121.2 ± 9.98 µg N_2O-N m^{-2} h^{-1}) compared to less frequently grazed sites (45.2 ± 6.92 µg N_2O-N m^{-2} h^{-1}) at the significance level of $P < 0.001$ (Figure 11A). The annual flux of frequently grazed sites ranged from 8.57 ± 2.70 to 12.55 ± 2.83 kg N_2O-N ha^{-1} y^{-1}, whereas at less frequently grazed sites the range was 2 ± 3.51–4.3 ± 2.63 kg N_2O-N ha^{-1} y^{-1}. Similarly, the N_2O EF from frequently grazed and less frequently grazed sites ranged from 1.14 to 3.07 and 1.02 to 2.34%, respectively.

Soil Type and N_2O Fluxes

There was a large difference in N_2O fluxes between soil types: free draining brown and grey brown podzols had higher N_2O emissions than poorly drained gley soils at the significance level of P less than 0.002 (Figure 9B). The N_2O emissions were much higher from brown and grey brown podzols (108.42 ± 10.15 µg N_2O-N m^{-2} h^{-1}) than gleys (70.0 ± 9.67 µg N_2O-N m^{-2} h^{-1}).

Discussion

N_2O Fluxes and Effect of N-Input

The instantaneous N_2O fluxes had large temporal variation within each site and between sites, depending on the weather conditions, soil type and management practices. The higher emission values were associated with N fertilizer applications (inorganic and organic) (Figure 4) and grazing practices. The rate, type and timing of applications of N fertilizer and grazing are important management factors affecting the potential for N_2O losses (Eckard and others 2010). Lower emissions were found in winter and early spring periods of both years. Higher emissions occurred in the summer and autumn, if weather conditions (such as WFPS) enabled fluxes. The sites CK, D and CF are characterized by a higher number of N_2O peaks than all other sites as they were subjected to more frequent N applications. The ranges of fluxes found in this study are similar to those observed by Flechard and others (2007) and Hyde and others (2006).

About 61% of the total N_2O emission is attributed to background emissions (Figure 7). Background N_2O emissions most likely occur because of nitrification followed by mineralization of soil organic N especially after rainfall events. Similar results have been reported in other studies (for example, Flessa and Russer 2002). The lowest annual N_2O flux was found at site SH2 and this is considered to be due to the combined effects of water logging (gley soil type) and less N-input, whereas lower N_2O fluxes at site SH1 are likely due to the significant clover fraction as clover helps to fix atmospheric N (Rasmussen and others 2008). Ledgard and others (2009) reported an experiment in the Netherlands, in which N_2O emissions from clover/grass plots was compared with that from grass-only plots. They reported that the emissions factor from clover-N was 0.2%, compared to 1.3% for fertilizer-N. The N_2 fixation by clover ranges from about 10 to 300 kg N ha^{-1} y^{-1} and it depends on a number of other factors including soil type,

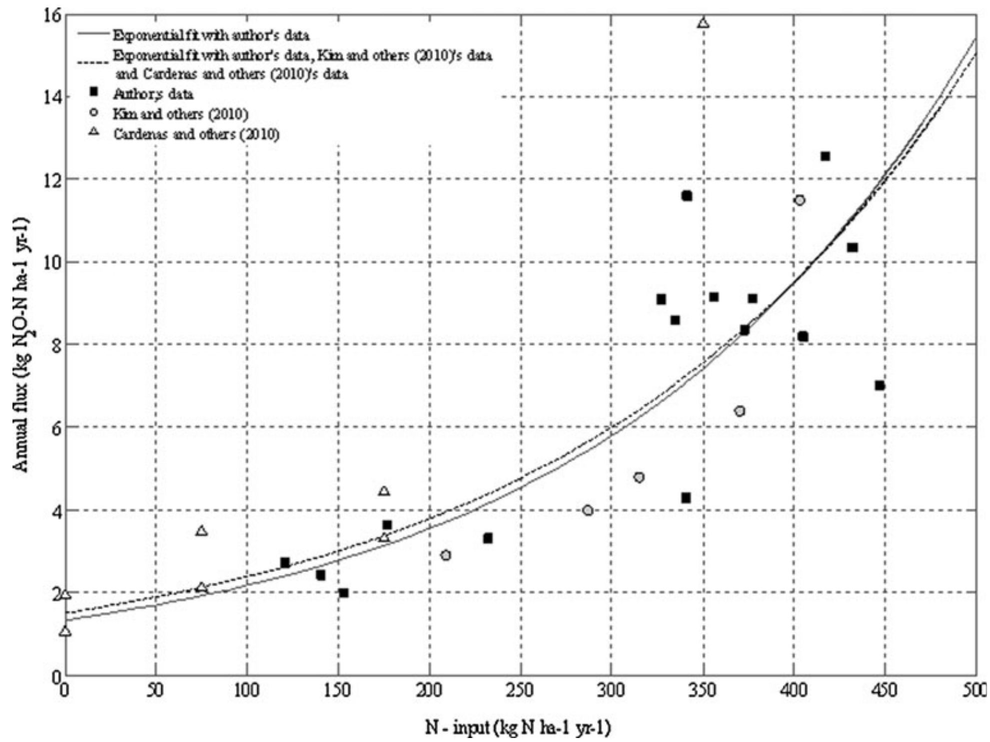

Figure 8. Exponential relationship between the annual N_2O flux and total N-input across eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)]. $F = 1.33 \times e^{[0.0046 \times \text{N-Input}]}$, where F is the annual N_2O flux and N-input is the total N applied in the field. For the combined data (data from this study; Kim and others 2010; Cardenas and others 2010) the exponential equation is $F = 1.50 \times e^{[0.0046 \times \text{N-Input}]}$ with $R^2 = 0.80$.

climate conditions and nutrient supply (Ledgard and others 2009). This fixed N becomes available to the grass after it is released into soil via exudates from living legume roots. The N_2O flux from site D is lower than CF, CK and PK, although it is intensively managed and frequently grazed. This lower emission is likely due to regular water logged conditions of that site causing a more difficult pathway for gaseous N_2O through water saturated soils when compared to more aerated soils at the other sites.

Negative flux values were mostly observed at the control sites (0N) which are due to the soils acting as an N_2O sink especially when soil moisture was high (Flechard and others 2005). One of the properties of N_2O is that it is easily dissolved in water. Therefore, when soil is wet it may be denitrified by microbes to N_2 or dissolved in the subsoil solution and be out gassed in drainage water and cause pollution of soil and water (Beauchamp 1997). Some of the fertilizer and manure that volatizes to NO_x and NH_3 soon after application is deposited on nearby soil and provides the substrate for nitrification and denitrification. This phenomenon was likely to have occurred at the BH, SH1 and SH2 sites which were extensively managed.

In general, it is considered that there is a linear relationship between N_2O emission and N-input in various N managed agricultural areas. This concept is used for current IPCC Tier I emission factor methodology which has adopted an emission factor of 1.25%. In this study, however, it was found that there was a nonlinear exponential relationship between N_2O emissions and N-input (Figure 8). It is estimated that when total N-input is less than approximately 300 kg N ha^{-1} y^{-1}, the annual N_2O flux is less than 5.0 kg N_2O-N ha^{-1} y^{-1}, but when the total N-input exceeds 300 kg ha^{-1} y^{-1}, a larger annual N_2O flux was observed which ranged between 5.0 and 12.6 kg N_2O-N ha^{-1} y^{-1}. Although several studies in the literature have reported a linear relation between N-input and N_2O emissions, for example, van Beek and others (2010) and Flechard and others (2007), a non-linear relationship is not common. For example, Cardenas and others (2010) measured N_2O emissions from fertilized grazed grasslands and found that N_2O emissions increased progressively when increasing N-input exceeded the

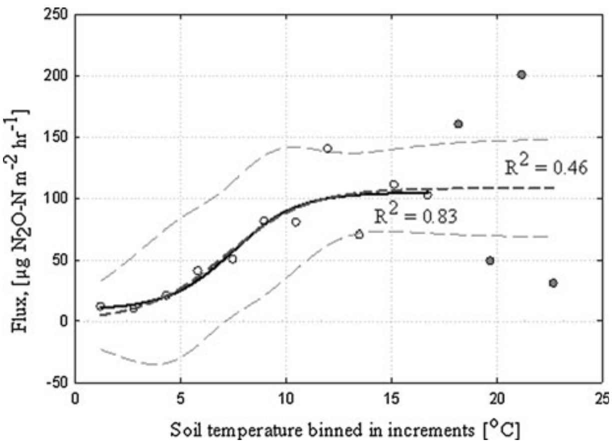

Figure 9. Sigmoidal relation (S-shaped) with 95% confidence interval of binned mean daily temperature (Soil T) and corresponding N_2O fluxes across eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)]. The $R^2 = 0.83$ is for the temperature range between 0 and 17°C, whereas $R^2 = 0.46$ is for the whole temperature range.

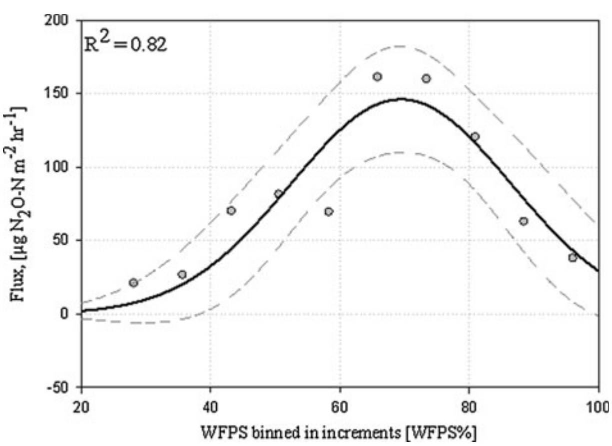

Figure 10. Gaussian relation (bell-shaped) with 95% confidence interval of binned mean daily water filled pore space (WFPS%) and corresponding N_2O fluxes across eight grassland sites in Ireland [Ballinhassig (BH), Clonakilty (CK), Donaghmore (D), Caaraig na bhFear (CF), Pallaskenry (PK), Kilworth (KW), Solohead1 (SH1) and Solohead2 (SH2)].

crop N demand. Similarly, in a modelling study, Eckard and others (2006) predicted that annual N_2O emissions increase exponentially as the annual rate of N-input increased.

The results of this study were corroborated with other studies of N_2O emissions, for example, Kim and others (2010) reported largely stable N_2O emissions of 4-5 kg N_2O-N at the nitrogen

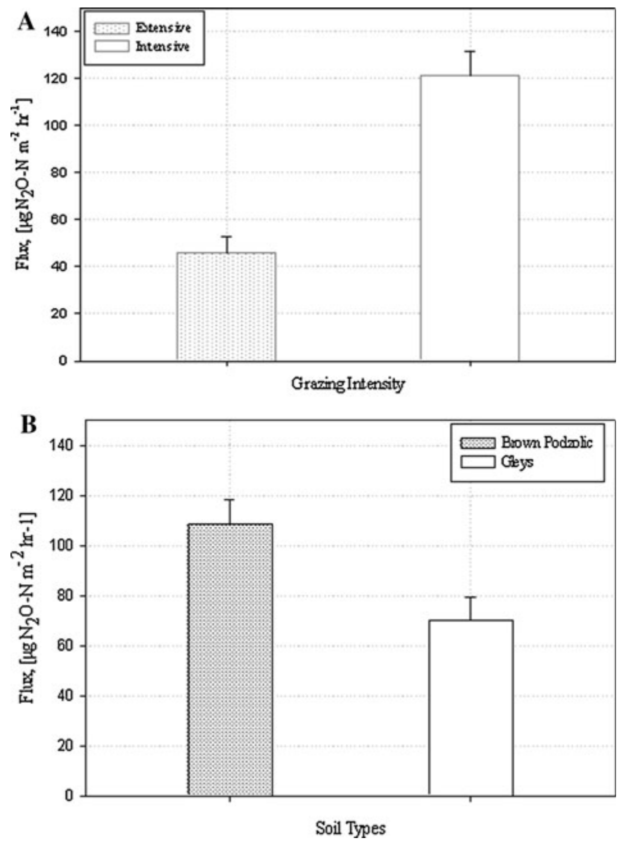

Figure 11. **A** Mean variation and standard deviations in N_2O fluxes between frequently ($n = 5$) and less frequently ($n = 3$) grazed sites and **B** mean variation and standard deviation in N_2O fluxes from podzols and gley soil in the south of Ireland.

application rates of 200–300 kg N-input ha^{-1}. At higher application rates of above 300 kg N ha^{-1}, significant increases in N_2O emissions were observed. Values of fluxes reported for other countries in Europe for application around 300 kg N ha^{-1} on grazed grasslands were 7–16 kg N_2O-N ha^{-1} y^{-1} for the Netherlands (Velthof and others 1996) and 5.9–22.3 kg N_2O-N for the UK (Cardenas and others 2010) which are in good agreement with this study.

These studies suggest that when excess N-input above the optimal agronomic requirement is applied, it decreases plant N uptake efficiency and residual N produces additional N_2O (for example, Grant and others 2006; Zebarth and others 2008). Several mechanisms may contribute to this effect. At larger N-input more mineral N is available to serve as a substrate for denitrifican and nitrification. Similarly, at large concentrations of NO_3^-, the N_2O:N_2 ratio of denitrification products increases. Van Groenigen and others (2010) noted that within the range of an N 'deficit' (defined as the balance between N application and aboveground biomass uptake), total N_2O emissions do not change significantly. This probably reflects the capacity of plants to take up a moderate rate of applied N (121-300 kg N ha^{-1} in this study) during their growth.

In Ireland, the maximum allowable total N application rate is approximately 500 kg N ha^{-1} y^{-1} which includes inorganic fertilizer N and organic N from livestock (slurry N and N deposited in the form of dung and urine) (European Directive 1991). In the present study, the maximum annual total N-input (organic and inorganic) was 442 kg N ha^{-1} y^{-1} which is less than the annual maximum N-input permissible under the Nitrate Directive value. Currently in Ireland the average farm stocking rate is 1.9 LU ha^{-1} (161.5 kg organic N ha^{-1}) and the average fertilizer use is 175 kg N ha^{-1} (Teagasc 2007) which is a total N-input of 336.5 kg N ha^{-1}. This means that currently in Ireland the total N-input is similar to our suggested value of 300 kg N $ha^{-1}$for reduced N_2O emissions.

To identify more precise fertilizer recommendations, agro-ecosystem specific relations between N_2O and yield would be helpful. This could be achieved through agro-ecosystem specific field experiments. The N_2O emissions show a significant relationship with N use efficiency. There are many agronomic indices of N use efficiency. For example, the 'recovery efficiency of applied N', which expresses the fraction of applied N taken up in the aboveground biomass at physiological maturity relative to a zero N treatment, can be helpful in translating our results into management practices. Furthermore, the belowground N recovery in the plants might have an additional value. Van Groenigen and others (2010) observed that N_2O emissions were reduced from 12.7 to 7.1 g N_2O-N kg^{-1} N uptake when N efficiency increased from 19 to 75%.

In the region of this study the range of DM production is 6.0–12.0 tonnes ha^{-1} y^{-1} (O'Donovan and others 2004). The lower value is typically associated with lower LU ha^{-1} and low N- application rates. In general, DM yield increases linearly in response to increasing N application rates from 25 to 350 kg N ha^{-1} (Frame 1992), decreasing to between 5 and 15 kg DM kg^{-1} N as N application rate increases from 350 to 450 kg N ha^{-1}. Response decreases until maximum DM yield is attained, and a point is reached where there may be no improvement in yield (O'Donovan and others 2004); the extra N may be lost through NO_3^- leaching and N_2O emissions and so on. This response to N application also depends on season, climatic conditions and grass growth rate. However, this response can be improved through many small applications of N rather than a few large applications (Saggar and others 2007). The frequent small applications can result in better distribution of grass growth across the growing seasons. The response to N application is greatest in late spring/early summer and poorest in very early spring and late autumn (Murphy and others 1986). The N application in early spring and late autumn can result in increased N_2O emissions (or other forms of N losses such as NO_3^- leaching) instead of grass growth because of more N available for N_2O production processes (O'Donovan and others 2004).

Nitrous oxide emission is strongly affected by the rate and timing of organic and inorganic N applications: N_2O emissions from slurry are higher when applied to wet soils than to drier soils and N_2O emissions are lower when N fertilizer is applied at least three days after the slurry application rather than at the same time (Eckard and others 2010). Similarly, the addition of N in small amounts at frequent intervals rather than a small number of large applications can also help in reducing N_2O emissions (Saggar and others 2007).

The calculated EFs (1.02–3.07%) are found to be in the range of that calculated by Hyde and others (2006) for the Wexford grassland (0.7–4.9%). Similarly, for Scottish grasslands Dobbie and Smith (2003a) reported EFs ranging from 1 to 3%. Our over all average EF is 69% higher than the IPCC default EF value of 1.25% which is still used by the Irish EPA for estimating Irish N_2O fluxes from grasslands. Therefore, it is suggested that the current IPCC (2006) emission factor method should consider the non-linear relationship between N-input and N_2O emission in grazed grasslands. Other authors also have criticized the IPCC value for either underestimating or overestimating the N_2O flux from applied N (Aabdalla and others 2009). Thus a wider approach is required which takes account of soil type, grazing regime, climatic conditions and agronomic indices which can ensure the applicability of a single EF for Ireland. The N application response with DM production can significantly improve the understanding of N_2O production in these sites.

The Effect of Soil Temperature on N_2O Fluxes

The daily soil temperature in this study ranged from 1.5 to 23°C. Most of the N_2O fluxes at soil temperatures less than 5°C were close to zero (Figure 9). The N_2O flux at 5°C was approximately 20 μg m^{-2} h^{-1}, but increased to 110 μg m^{-2} h^{-1} at 17°C. Nitrous oxide production at temperatures lower than 5°C is considered to be predominantly controlled by physical processes resulting in a release of N_2O during thawing after the soil has been frozen (Christensen and Tiedje 1990), although some authors have shown some biological activities at lower temperatures. Freezing of soil was absent in this study. At temperatures above 5°C, the N_2O emission is assumed to be dominated by biological activities as increased temperature enhances microbial activity (Scanlon and Kiely 2003). In this study, temperatures above 5°C are considered the most influencing. The N_2O cluster above 17°C is scattered (Figure 9) suggesting that temperature might not be the main factor influencing N_2O emissions above 17°C and higher emission may be attributed to other controlling parameters such as WFPS and N availability. This temperature response is similar to that obtained by Saggar and others (2004). These authors found a profound temperature effect on N_2O fluxes between 5 and 18 °C.

The Effect of Water Filled Pore Space on N_2O Emission

Below 40% WFPS, N_2O production was less than 35 μg m^{-2} h^{-1} but increased to 122 μg m^{-2} h^{-1} at 60% WFPS (Figure 10). Peak N_2O emissions occurred in the range of 60–80% WFPS with maximum emission at approximately 70% WFPS. Above 80% WFPS the N_2O flux decreased rapidly. The optimum WFPS may be the result of several biological and physical processes. Davidson and Verchot (2000) observed that nitrification occurs up to a WFPS of 60%. At WFPS greater than 60% denitrification becomes dominant (Lemke and others 1998). At high values of WFPS above 80%, oxygen diffusion may become restricted and hence the product of denitrification is primarily N_2 (Veldkamp and others 1998). Robertson and Tiedje (1988) suggested that denitrification can act as a sink as well as a source for N_2O. The most probable explanation of the peak N_2O emission between 60 and 80% WFPS is that it increased to a level where simultaneous denitrification and nitrification were at their maximum (70% WFPS). Above this WFPS, denitrification was the main process producing N_2O and as the soil is more anaerobic and N_2 emissions dominate N_2O. This response was found in other studies (for example, Arriaga and others 2010). However, the optimum water content for N_2O emission may differ from soil to soil (Bouwman 1998).

The Effect of Soil Type on N_2O Fluxes

When N_2O emissions from different soils were compared, brown podzolic and grey brown podzolic soils had higher emissions than gleys (Figure 11A). Podzols are considered well drained with high porosity, which can produce high N_2O emissions because of nitrification due to easy availability of O_2. In addition in this study these soils were intensively managed with frequent grazing. The gley soils are frequently water logged with anaerobic conditions, and very high WFPS, resulting in the lowest N_2O emissions. The NO_3^- leaching was not included in this study. As these emissions of NO_3^- are generally linked with higher N-input (Van Groenigen and others 2010), we expect that including those emissions might further strengthen this relationship found in this study.

The Effect of Grazing Frequency on N_2O Fluxes

Grazing can enhance N_2O production, as reported by Velthof and Oenama (1995). According to Oenema and others (1997), grazing enhances N_2O emissions due to the presence of active N hot spots as a result of dung and urine deposition. Grazing indirectly influences the soil fertility via induced changes in plant composition (Patra 2006), N cycling and consequently increased N_2O flux from soils (Aabdalla and others 2009). According to Nunez and others (2007) the nutrient cycle is influenced by grazing animals who can return as much as 80% of consumed N in the form of dung and urine. In our experiment intensively grazed sites produced up to three times higher hourly N_2O fluxes than extensively grazed sites (Figure 11B). This is most likely due to higher urine and dung excretions as well as soil compaction at the intensively grazed sites (CK, D, CF, PK and KW) by comparison to extensively grazed sites (BH, SH1 and SH2). Douglas and Crawford (1993) found that the N_2O emissions and total denitrification rates were up to two times higher in compacted grassland soil than in uncompacted grassland soils. Compaction which reduces soil porosity, increases soil density, reduces hydraulic conductivity and impedes root penetration is important in shifting soil conditions towards an anaerobic state at the same level of WFPS (Hyde 2004). Other studies, for example, Wolf and others (2010), found higher N_2O emissions with an increase in stocking rate (LU ha^{-1}) during the growing season.

Restricted grazing on seasonally wet soils not only reduces N-input from urine, but also reduces hoof compaction of the soil. Luo and others (2008) reported a total reduction of N_2O emission by 7–11% under restricted grazing regimes. Similarly, the application of the concept of carrying capacity (the number of animals that the pasture can support) can significantly reduce the N_2O losses from soils and the carrying capacity is determined by various other factors such as food supply, climate conditions and waste assimilation (Nunez and others 2007).

Conclusion

This study shows that the estimated annual N_2O flux from grasslands in southern Ireland was greater than those predicted by the IPCC default EF of 1.25%. The N_2O emissions in this experiment were dependent on N fertilizer application, grazing management, soil types and variations in soil temperature and WFPS. Peak emissions occurred in short periods following the fertilization and grazing events. A strong relationship was observed between N-input, soil temperatures, soil moisture and N_2O emissions. Soil temperatures between 5 and 17°C were optimum for N_2O emission. Similarly, WFPS was found to be influencing in the range of 60–80%. Frequently grazed sites produced N_2O emissions three times higher than less frequently grazed sites.

The results of this study suggest that different management strategies can reduce anthropogenic N_2O emissions including: (1) the N application should be less than 300 kg ha^{-1} and this will significantly reduce emissions; however, agro-ecosystem specific requirements for optimum grass production should be part of the determining procedure; (2) the reduction of N application would be most effective in intensively managed sites (CK, D, CF, PK, KW) which received more than 300 kg N ha^{-1} rather than for extensive sites (BH, SH1 and SH2) which received less than 300 kg N ha^{-1} and (3) restricted grazing on seasonally wet soils especially from intensively grazed sites, for example, CK, D, CF, PK and KW, can also significantly reduce N_2O emissions.

This study shows that the IPCC default EF underestimates the fluxes. Further study on a wider range of grazing regimes, plant biomass production and soil types should be carried out.

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References

Abdalla M, Jones M, Smith P, Willaims M. 2009. Nitrous oxide fluxes and denitrification sensitivity to temperature in Irish pasture soils. Soil Use Manag 24:376–88.

Anon. 2006. S.I. No. 378/2006. European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2006. Department of Environment, Heritage and Local Government. Dublin, Ireland. http://www.environ.ie/en/ (20 July, 2010).

Arriaga H, Salcedo G, Calsamigila S, Merino P. 2010. Effect of diet manipulation in dairy cow N balance and nitrogen oxides emissions from grassland in northern Spain. Agric Ecosyst Environ 135:132–9.

Barton L, Kiese R, Gatter D. 2008. Nitrous oxide emissions from a cropped soil in a semi-arid climate. Glob Change Biol 14:177–92.

Beauchamp EG. 1997. Nitrous oxide emissions from agricultural soils. Can J Soil Sci 77:113–23.

Bouwman AF. 1998. Nitrogen oxides and tropical agriculture. Nature 392:866–7.

Cardenas LM, Thorman R, Ashlee N, Butler M et al. 2010. Quantifying annual N_2O emissions fluxes from grazed grassland under a range of inorganic fertilizer nitrogen input. Agric Ecosyst Environ 136:218–26.

Christensen S, Tiedje JM. 1990. Brief and vigorous nitrous oxide production by soil at spring thaw. J Soil Sci 41:1–4.

Clough TJ, Sherlock RR, Rolston DE. 2005. A review of the movement and fate of N_2O in the subsoil. Nutr Cycl Agroecosyst 72:3–11.

Davidson EA, Savage K. 2002. Minimizing artifacts and biases in chamber-based measurements of soil respiration. Agric For Meteorol 113:21–37.

Davidson EA, Verchot LV. 2000. Testing the hole in pipe model of nitric oxide emissions from soils using the TRAGNET database. Global Biogeochem Cycles 14:1035–43.

Dobbie KE, Smith KA. 2003a. 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.

Dobbie KE, Smith KA. 2003b. Impact of different forms of fertilizer on N2O emissions from intensive grassland. Nutr Cycl Agroecosyst 67:37–46.

Douglas JT, Crawford CE. 1993. The response of a ryegrass sward to wheel traffic and applied nitrogen. Grass Forage Sci 48:91–100.

Eckard RJ, Johnson I, Champon DF. 2006. Modelling nitrous oxide abatement strategies in intensive pasture systems. Int Congr Serv 1293:76–85.

Eckard RJ, Grainger C, de Klein, CAM. 2010. Options for the abatement of methane and nitrous oxide from ruminant production: a review. Livestock Science. doi:10.1016/jlivsci.2010.02.010.

EPA. 2009. Irish Environmental Protection Agency, 2008. http://www.epa.ie (accessed on 20 July 2010).

European Council. 1991. Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources. Off J Eur Union L 375(31/12/1991): 1–8.

FAO. 2004. FAOSTAT database collections. Food and Agriculture Organization, Rome, Italy. www.apps.fao.org.

Flechard CR, Neftel A, Jocher M, Christof A, Jurg F. 2005. Bidirectional soil/atmosphere N_2O exchange over two mown grassland systems with contrasting management practices. Glob Change Biol 11:2114–27.

Flechard CR, Ambus P, Skiba U, Rees RM, Hensen A, Amstel A, Dasselaar AP, Soussana JF, Jones M, Clifton-Brown J, Raschi A, Horvath L, Neftel A, Joscher M, Ammann C, Leifeld J, Fuhrer J, Calanca P, Thalman E, Pilegaard L, Di Marco C, Campbell C, Nemitz E, Hargreaves KJ, Levy PE, Ball BC, Jones SK, van de Bulk WCM, Groot T, Blom M, Domingues R, Kasper G, Allar A, Caschia E, Cellier P, Laville P, Henault C, Bizouard F, Abdalla M, Williams M, Baronti S, Berretti F, Grosz B. 2007. Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe. Agric Ecosyst Environ 121:135–52.

Flessa H, Russer R. 2002. N_2O and CH_4 fluxes in potato fields: automated measurement, management effects and temporal variation. Geoderma 105:307–25.

Frame J. 1992. Improved grassland management. Ipswich: Farming Press Books.

Grant RF, Pattey E, Goddard TW, Kryzonowski LM, Puurveen H. 2006. Modeling the effects of fertilizer application rate on nitrous oxide emissions. Soil Sci Soc Am J 70:235–48.

Holland EA, Robertson GP, Greenberg J. 1999. Soil CO_2, N_2O & CH_4 exchange. In: Robertson GP, Ed. Standard soil methods for long-term ecological research. Oxford: Oxford University Press. p 185–202.

Hsieh CI, Leahy P, Kiley G, Li C. 2005. The effect of future climate perturbation on N2O emissions from fertilized humid grassland. Nutr Cycl Agroecosyst 73:15–23.

Hyde BP. 2004. Nitrous oxide emission from Irish grassland, PhD thesis, University College Dublin, Ireland.

Hyde BP, Hawkins MJ, Fanning AF, Noonan D, Ryan M, Toole PO, Carton OT. 2006. Nitrous oxide emissions from a fertilized and grazed grassland in South East of Ireland. Nutr Cycl Agroecosyst 75:187–200.

IPCC. 2001. Climate change 2001: The scientific basis. Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press.

IPCC. 2006. Climate Change 2006: Guidelines for National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change (IPCC), Institute for Global Environmental Strategies Hayama, Kanagawa, Japan, 240-0115

IPCC. 2007. Climate change 2007: The physical Science Basis. Summary for Policy makers. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. 21 p.

Kim D, Michael M, Kiely G. 2010. Effect of increased N use dry periods on N_2O emission from fertilized grassland. Nutr Cycl Agroecosyst. doi:10.1007/s10705-010-9365-5.

Ledgard S, Schils R, Eriksen J, Lou J. 2009. Environmental impacts of grazed clover/grass pastures. Ir J Agric Food Res 48:209–26.

Lemke RL, Izaurralde RC, Nyborg M. 1998. Seasonal distribution of nitrous oxide emissions from soils in the parkland region. Soil Sci Soc Am J 62:1320–6.

Luo J, Ledgard SF, Lindsey SB. 2008. A test of winter farm management option for mitigation nitrous oxide emissions from a dairy farm. Soil Use Manage 24:121–30.

Murphy PM, Turner S, Murphy M. 1986. Effect of spring applied urea and calcium ammonium nitrate on white clover (Trifolium repens) performance in a grazed ryegrass-clover pasture. Ir J Agric Res 25:251–9.

Nunez P, Demanet R, Matus F, Mora ML. 2007. Grazing management, ammonia and nitrous oxide emissions: a general view. R.C. Suelo Nutr 7:61–99.

O'Donovan M, Delaby L, Stakelum G, Dillon P. 2004. Effect of Autumn/spring nitrogen application date and level on DM production and N efficiency in perennial ryegrass swards. Ir J Agric Food Res 43:31–41.

Oenema O, Velthof GL, Yamulki S, Jarvis SC. 1997. Nitrous oxide emissions from grazed grassland. Soil Use Manage 13:288–95.

Patra AK, Abbadie L, Clays A, Degrange V, Grayston SJ, Guillaumaud N, Loiseau P, Louault F, Mahmood S, Nazaret S, Philippot L, Poly F, Prosser JI, Le Roux X. 2006. Effects of management regime and plant species on the enzyme activity and genetic structure of N-fixing, denitrifying and nitrifying bacterial communities in grassland soils. Environ Microbiol 8:1005–16.

Rasmussen J, Gjettermann B, Eriksen J, Jensen ES, Hogh-Jensen H. 2008. Fate of ^{15}N and ^{14}C from labelled plant material: Recovery in perennial ryegrass–clover mixtures and in pore water of the sward. Soil Biol Biochem 40:3031–9.

Robertson GP, Tiedje JM. 1988. Deforestation alters denitrification in a lowland tropical rain forest. Nature 336:756–9.

Saggar S, Andrew RM, Tate KR, Hedley CB et al. 2004. Modelling nitrous oxide emissions from New Zealand dairy grazed pastures. Nutr Cycl Agroecosyst 68:243–55.

Saggar S, Giltrap DL, Li C, Tate KR. 2007. Modelling nitrous oxide emissions from grazed grassland in New Zealand. J Agric Ecosys Environ 119:205–16.

Samarkin VA, Madigan MT, Bowles MW, Casciotti KL, Priscu JC, McKay CP, Jpye SB. 2010. Abiotic nitrous oxide emissions from the hypersaline Don Juan Pond in Antarctica. Nature 3:341–4.

Scanlon TM, Kiley G. 2003. Ecosystem-scale measurements of nitrous oxide fluxes for an intensely grazed, fertilized grassland. Geophys Res Lett 30. doi:10.1029/2003GL017454.

Schmidt U, Thoni H, Kaupenjohann M. 2000. Using a boundary line approach to analyze N_2O flux data from agricultural soils. Nutr Cycl Agroecosyst 57:119–29.

Skiba UM, Sheppard LJ, MacDonald J, Fowler D. 1998. Some key environmental variables controlling nitrous oxide emissions from agricultural and semi-natural soils in Scotland. Atmos Environ 32:3311–20.

Teagasc. 2007. National Farm Survey. Athenry: Teagasc.

Teagasc. 2009. The Irish Agriculture and Food Development Authority, 2009. http://www.teagasc.ie.

Van Beek CL, Pleijter M, Jacobs CMJ, Velthof GL, van Groenigen JW, Kuikman PJ. 2010. Emissions of N_2O from fertilized and grazed grassland on organic soil in relation to groundwater level. Nutr Cycl Agroecosyst 86:331–40.

Van Groenigen JW, Velthof GL, Oenema O, van Groenigen KJ, Van Kessel C. 2010. Towards an agronomic assessment of N_2O

emissions: a case study on arable crops. Eur J Soil Sci 61:903–13.

Veldkamp E, Keller M, Nunez M. 1998. Effects of pasture management on N2O and NO emissions from soils in the humid tropics of Costa Rica. Global Biogeochem Cycles 12:71–9.

Velthof GL, Brader AB, Oenema O. 1996. Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands. Plant Soil 181:263–74.

Velthof GL, Oenema O. 1995. Nitrous oxide fluxes from grassland in the Netherlands: effects of soil type, nitrogen fertilizer application and grazing. Eur J Soil Sci 46:541–9.

Watson CJ, Foy RH. 2001. Environmental impacts of nitrogen and phosphorus cycling in grassland systems. Outlook Agric 30:117–27.

Wolf B, Zheng X, Bruggemann N, Chen W et al. 2010. Grazing-induced reduction of natural nitrous oxide release from continental steppe. Nature 464:881–4.

Zebarth BJ, Rochette P, Burton DL. 2008. N2O emissions from spring barley production as influenced by fertilizer nitrogen rate. Can J Soil Sci 88:197–205.