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Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe

C.R. Flechard [a,*], P. Ambus [b], U. Skiba [c], R.M. Rees [d], A. Hensen [e], A. van Amstel [f], A. van den Pol-van Dasselaar [g], J.-F. Soussana [h], M. Jones [k], J. Clifton-Brown [l], A. Raschi [m], L. Horvath [o], A. Neftel [a], M. Jocher [a], C. Ammann [a], J. Leifeld [a], J. Fuhrer [a], P. Calanca [a], E. Thalman [a], K. Pilegaard [b], C. Di Marco [c], C. Campbell [c], E. Nemitz [c], K.J. Hargreaves [c], P.E. Levy [c], B.C. Ball [d], S.K. Jones [d], W.C.M. van de Bulk [e], T. Groot [e], M. Blom [e], R. Domingues [f], G. Kasper [g], V. Allard [h], E. Ceschia [h], P. Cellier [i], P. Laville [i], C. Henault [j], F. Bizouard [j], M. Abdalla [k], M. Williams [k], S. Baronti [m], F. Berretti [m], B. Grosz [n]

[a] Agroscope Reckenholz-Tänikon, Research Station ART, Air Pollution/Climate Group, Reckenholzstrasse 191, CH-8046 Zurich, Switzerland
[b] RISØ National Laboratory, P.O. Box 49, 4000 Roskilde, Denmark
[c] CEH, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian EH26 0QB, Scotland, United Kingdom
[d] SAC, King's Buildings, West Mains Road, Edinburgh EH9 3JG, Scotland, United Kingdom
[e] ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands
[f] WUR, Environmental Systems Analysis Group, P.O. Box 9101, 6700 HB Wageningen, The Netherlands
[g] WUR, Animal Sciences Group, P.O. Box 65, 8200 AB Lelystad, The Netherlands
[h] INRA, UR874 Grassland Ecosystem Research, 234, Avenue du Brézet, 63100 Clermont-Ferrand, France
[i] INRA, INA P-G, UMR1091 Environnement et Grandes Cultures, 78850 Thiverval-Grignon, France
[j] INRA, UMR Microbiologie des Sols, 17, rue Sully, BP 86510, 21065 Dijon Cedex, France
[k] TCD (Trinity College Dublin), Dublin 2, Ireland
[l] IGER, Plas Gogerddan, Aberystwyth SY23 3EB, Wales
[m] IATAA, Piazzale delle Cascine 18, 50144 Firenze, Italy
[n] ELU (Eotvos Lorand University), Pazmany P. s. 1/A, 1177 Budapest, Hungary
[o] HMS (Hungarian Meteorological Service), Gilice 39, 1181 Budapest, Hungary

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Abstract

Soil/atmosphere exchange fluxes of nitrous oxide were monitored for a 3-year period at 10 grassland sites in eight European countries (Denmark, France, Hungary, Ireland, Italy, The Netherlands, Switzerland and United Kingdom), spanning a wide range of climatic, environmental and soil conditions. Most study sites investigated the influence of one or several management practices on N_2O exchange, such as nitrogen fertilization and grazing intensity. Fluxes were measured using non-steady state chambers at most sites, and alternative measurement techniques such as eddy covariance and fast-box using tunable diode laser spectroscopy were implemented at some sites. The overall uncertainty in annual flux estimates derived from chamber measurements may be as high as 50% due to the temporal and spatial variability in fluxes, which warrants the future use of continuous measurements, if possible at the field scale. Annual emission rates were higher from intensive than from extensive grasslands, by a factor 4 if grazed (1.77 *versus* 0.48 kg N_2O-N ha^{-1} $year^{-1}$) and by a factor 3 if ungrazed (0.95 *versus* 0.32 kg N_2O-N ha^{-1} $year^{-1}$). Annual emission factors for fertilized systems were highly variable, ranging from 0.01% to 3.56%, but the mean emission factor across all sites (0.75%) was substantially lower than the IPCC default value of 1.25%. Emission factors for individual fertilization events increased with soil temperature and were generally higher for water-filled pore space values in the range 60–90%, though precipitation onto dry soils was also shown to lead to high losses of N_2O-N from applied fertilizer. An empirical, multiple

* Corresponding author. Tel.: +41 1 377 7511; fax: +41 1 377 7201.
E-mail address: chris.flechard@art.admin.ch (C.R. Flechard).

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regression model to predict N_2O emission factors on the basis of soil temperature, moisture and rainfall is developed, explaining half of the variability in observed emission factors.

Keywords: Nitrous oxide; N_2O flux; Grassland; Grazing; Fertilizer; Emission factor

1. Introduction

The atmospheric greenhouse gas nitrous oxide (N_2O) is currently believed to contribute a radiative forcing of 0.15 W m^{-2}, i.e. about 6% of the combined forcing (2.43 W m^{-2}) attributed to the increases in the abundance of the well-mixed greenhouse gases from pre-industrial to the present time (IPCC, 2001a). This places N_2O as the fourth highest single forcing influence behind carbon dioxide (CO_2), methane (CH_4) and the halocarbon CFC-12. The rise in tropospheric N_2O concentrations from pre-industrial values of around 270 ppbv to the level of 314 ppbv in 1998 (Machida et al., 1995; Flückiger et al., 1999) is a consequence of increased N_2O emissions from both natural and agricultural ecosystems, driven by increased fertilizer use, dinitrogen (N_2) fixation and atmospheric N deposition (Smith et al., 1997; Skiba et al., 1998). Soils are the dominant source of N_2O worldwide, releasing an estimated 9.5 Tg N_2O-N $year^{-1}$ to the atmosphere (65% of global N_2O emissions), of which 3.5 Tg N_2O-N $year^{-1}$ originate in agricultural soils and 1 Tg N_2O-N $year^{-1}$ in temperate grasslands (IPCC, 2001a).

The major processes leading to N_2O evolution are aerobic autotrophic nitrification – the stepwise oxidation of ammonia (NH_3) to nitrite (NO_2^-) and to nitrate NO_3^- – and anaerobic heterotrophic denitrification – the stepwise reduction of NO_3^- to NO_2^-, nitric oxide (NO), N_2O and ultimately N_2 – where facultative anaerobe bacteria use NO_3^- as an electron acceptor in the respiration of organic material when molecular oxygen (O_2) is in short supply (Davidson, 1991). Both types of processes are carried out by bacteria in soils, sediments, water bodies and also in wastewater treatment facilities. Other N_2O production mechanisms include heterotrophic nitrification, more common in fungi than in bacteria (Odu and Adeoye, 1970) and aerobic denitrification by the same heterotrophic nitrifiers (Robertson and Kuenen, 1990); fungal denitrification, where N_2O is the final product as many fungi lack the N_2O-reductase enzyme to further reduce N_2O-N_2 (Laughlin and Stevens, 2002); nitrifier denitrification, which is carried out by autotrophic NH_3-oxidizing bacteria (Wrage et al., 2001); and chemodenitrification, which is the non-biological reaction of the intermediate products of nitrification with organic or inorganic soil compounds (Chalk and Smith, 1983). An important factor underpinning all the above process is the mineralization of soil organic matter, which contributes to the soil pool of available N through the release of NH_3/NH_4^+ (Bouwman et al., 2002).

The net N_2O exchange flux between soil and the atmosphere results from the balance of concurrent production and consumption mechanisms within the soil. The nature and strength of the soil N_2O source depend heavily on soil moisture, since this controls the degree of aeration and O_2 content and thus determines whether nitrification or denitrification prevails (Smith et al., 2003). Nitrous oxide emissions are believed to peak at intermediate soil water-filled pore space (WFPS) values, in the range 50–70% (Davidson, 1991); in drier soils nitrification is inhibited, while in water-logged soils complete denitrification favours N_2 evolution. Soil mineral N and temperature provide two other major controls on N_2O production (Smith et al., 2003; Conen et al., 2000; Skiba et al., 1998). Anaerobic heterotrophic denitrification is conventionally regarded as the only biological sink for N_2O in soils (Conrad, 1996) but little is known about non-biological sinks (Davidson, 1991). Beside microbiological processes, the movement and fate of N_2O produced in the subsoil are mainly determined by molecular diffusion, convection, ebullition and entrapment, which are themselves dependent on soil temperature, WFPS, precipitation and other meteorological variables (Clough et al., 2005).

In Europe, semi-natural and managed grasslands are commonly used to provide ruminants with fodder, either directly in the field during the grazing season, or as hay and silage during the winter. As nitrogen (N) is often limiting in grassland ecosystems, mineral (e.g. ammonium nitrate, AN) or organic (e.g. farmyard manure, cattle slurry) fertilizers are frequently applied to increase herbage productivity. However, available N may temporarily exceed plant needs and N-losses then occur through leaching of NO_3^- to groundwater and through gaseous emissions of ammonia (NH_3), NO and N_2O, even when timing and amounts of N-fertilization are optimized. Nitrous oxide emissions from grasslands thus tend to occur in short-lived bursts following the application of fertilizers (Leahy et al., 2004; Clayton et al., 1997; Ryden, 1981), and the small-scale spatial variability in fluxes is notoriously high (Ambus and Christensen, 1994; Ball et al., 2000). Thus, besides the technical and analytical challenges inherent in chamber or eddy correlation (EC) flux measurements, temporal and spatial variations contribute large sources of uncertainty in N_2O fluxes at the field and annual scales (Flechard et al., 2005).

To better understand and quantify processes controlling N_2O emissions from temperate grasslands, we examine in this paper the N_2O flux monitoring datasets collected over 3 years at 10 grassland sites in eight European countries within the framework of the European Union GREENGRASS project (2002–2004). The study sites spanned a wide range of soil, climatological and environmental conditions as well as of management practices, and thus afforded a unique opportunity of re-assessing our present knowledge of grasslands as sources of N_2O. Emission factors (EFs) from added fertilizer are calculated and their relationships to major environmental controlling variables are examined. This paper represents the synthesis of a collective N_2O flux monitoring effort within the GREENGRASS network. As a result, parts of the datasets showed or mentioned here have been previously published elsewhere as individual contributions by individual groups (Allard et al., 2007; Di Marco, 2005; Flechard et al., 2005; Jones et al., 2007), while the present paper offers an original overview from a more general perspective.

2. Materials and methods

An overall and general description of materials and methods within the project is given here; for more details on specific sites, the reader is referred to publications by the various groups (e.g. Allard et al., 2007; Di Marco, 2005; Flechard et al., 2005; Jones et al., 2007).

2.1. Study sites

The measurement stations of the GREENGRASS network were selected to be representative of the major grassland types of Western and Central Europe. The sites are broadly distributed along a NW through SE gradient, from the British Isles and Scandinavia to Italy and Hungary (http://www.clermont.inra.fr/greengrass/), thus covering most European climatological zones from temperate wet oceanic to dry continental. A vertical gradient is also described from the lowlands of The Netherlands and Denmark to the volcanic highlands of Central France and south to the Italian Alps (Table 1A). While the underlying soils are naturally diverse (Table 1B), grassland management practices reflect the socio-economic environment as well as climate, soil and vegetation. The effect of grassland extensification/intensification was studied at four sites in

Table 1A
Measurement sites

Abbreviation[a]	Site full name	Country	Coordinates		Elevation m (a.s.l.)	Mean annual	
			Latitude	Longitude		Air temperature (°C)	Rainfall (mm)
Hu-BG	Bugac-Puszta	Hungary	46°41′30″N	19°36′06″E	140	10.5	500
UK-BS	Easter Bush	Scotland	55°52′N	3°2′W	190	8.8	638
Ei-CA	Carlow	Ireland	52°51′59″N	6°54′30″W	56	9.4	824
UK-CP	CowPark	Scotland	55°52′N	3°12′W	200	8.6	849
Fr-LA	Laqueuille	France	45°38′35″N	2°44′9″E	1040	8.0	1313
Nl-LE	Lelystad	The Netherlands	52°30′N	5°30′E	−5	10.0	780
Dk-LV	Lille Valby	Denmark	55°41′40″N	12°07′07″E	15	9.2	731
It-MA	Malga Arpaco	Italy	46°07′00″N	11°42′10″E	1699	6.3	1200
CH-OE	Oensingen	Switzerland	47°17′N	07°44′E	450	9.0	1109
UK-PO	Poldean	Scotland	55°17′22″N	3°24′08″W	196	8.0	798

[a] The first two letters stand for the country, the last two letters for the site name.

Table 1B
Soil characteristics

Site abbreviation	Soil type	% Sand[a]	% Silt[a]	% Clay[a]	Depth of main rooting zone (m)	Bulk density[a] (kg soil l^{-1} dry soil)	Total pore space[a] ($m^3\ m^{-3}$)	Soil C ($mg\ g^{-1}$)	C/N (ratio)	pH
Hu-BG	Sandy	60	20	20	0.25	1.18	0.55	55[b]	16.0	7.7
UK-BS	Gleyic cambisol	53	26	20	0.31	1.22	0.54	32[b]	13.7	5.1
Ei-CA	Calci-gleyic luvisol, medium texture	51	27	22	0.20	1.07	0.60	39[c]	10.0	7.3
UK-CP	Gleysol	41	34	25	0.30	1.22	0.48	38[b]	14.1	6.4
Fr-LA	Basaltic andosol	27	56	18	0.07	0.64	0.76	80[c]	10.7	5.3
Nl-LE	Fluvisol	37	35	27	0.20	nd	0.65	22[c]	10.5	7.4
Dk-LV	Loamy umbrisol	45	37	18	0.07	1.51	0.43	14[b]	9.4	6.8
It-MA	Typic Hapludalfs, fine loamy	68	22	10	0.15	1.15	0.52	30[b]	10.5	5.5
CH-OE	Stagnic cambisol (eutric)	22	35	43	0.30	1.10	0.58	24[b]	9.7	7.5
UK-PO	Orthic podsol	nd	nd	nd	0.10	0.40	0.85	186[b]	nd	nd

[a] Average within the layer 0–10 cm; nd: not determined.
[b] Total soil C.
[c] Soil organic C.

Table 1C
Site management and nitrogen inputs

Site[a]	Vegetation type/age of grassland	Management intensity	Grazing (continuous/ rotational) LSU ha^{-1}[b]	Ruminant type	Cuts[b] ($year^{-1}$)	Fertilization (kg N ha^{-1} $year^{-1}$)[b]	Fertilizer type	Atmospheric N deposition[c] (kg N ha^{-1} $year^{-1}$)
Hu-BGc	Semi-arid semi-natural grassland (>150 years)	Extensive	None	–	0	0	–	7
Hu-BGg	Semi-arid semi-natural grassland (>150years)	Extensive	0.5 (cont. January–October)	Cattle	0	0	–	7
UK-BS	>90% *Lolium perenne* (>20 years)	Intensive	1–2 (cont. whole year)	Cattle/Sheep	1–2	200	NPK/AN	9
Ei-CA	*Lolium perenne*, *Trifolium repens* (estab. 2001)	Intensive	2 (cont. July–November)	Cattle	1	200	CAN	11
UK-CPe	*Lolium perenne*	Extensive	None	–	2–3	0	–	9
UK-CPi	*Lolium perenne*	Intensive	None	–	2–3	300	AN (none in 2004)	9
Fr-LAe	*Lolium perenne, Trifolium pratense, Taraxacum officinale, Poa* (>40 years)	Extensive	1 (cont. April–September)	Cattle	0	0	–	14
Fr-LAi	*Lolium perenne, Trifolium pratense, Taraxacum officinale, Poa* (>40 years)	Intensive	2 (cont. April–September)	Cattle	0	175	AN	14
Nl-LE	*Lolium perenne*, *Taraxacum officinale* (10 years)	Intensive	16 (rota. May–September)	Cattle	2–4	300	CAN + cattle slurry	17
Dk–LV1	*Lolium perenne* (estab. 1998)	Intensive	None	–	2	200	NPKS + horse manure	13
Dk-LV2	Barley (*Hordeum vulgare*) until 2003, then grassland	Intensive	None	–	1	200	NPKS + horse manure	13
It-MA	*Arrhenatheretum elatioris*	Extensive	Cont. June–September	Cattle	0	90	AN (only in 2003)	21
CH-OEe	Grass-clover mixture (30 spp) (estab. 2001)	Extensive	None	–	3	0	–	15
CH-OEi	Grass-clover mixture (7 spp) (estab. 2001)	Intensive	None	–	4	200	AN + cattle slurry	15
UK-PO	*Lolium perenne, Festuca spp* (>35 years)	Intensive	1.5 (cont. whole year)	Cattle/Sheep	0	50	AN	9

[a] Suffixes c, e, g, and i stand for "control", "extensive", "grazed" and "intensive", respectively.
[b] Mean values over the period 2002–2004.
[c] Sum of total dry + wet deposited reduced and oxidized N compounds. *Source*: EMEP Unified model revision 1.7, 50 km × 50 km grid (EMEP, 2003; http://www.emep.int/Model_data/model_data.html).

Table 2
N_2O flux measurement methods and overall results

Site	N_2O flux measurements (ng N_2O-N m^{-2} s^{-1})									Annual N_2O flux (kg N_2O-N ha^{-1} y^{-1})		EF (%)
	Method & analyzer (replicates)	Sampling frequency	N (Count)	Min	25%	Avc.	Med.	75%	Max	Flux integration Method	Flux	
Hu-BGc	Manual static chambers & GC (5 reps / field)	Bi-weekly	2002: 55	-0.1	0.3	9.1	4.1	6.5	37.9	Averaging of all data monthly	1.2	nd [1]
			2003: 130	-2.5	0.0	2.5	2.3	3.8	10.1		0.8	nd [1]
			2004: 120	-1.5	0.3	2.3	1.0	5.4	8.0		0.7	nd [1]
Hu-BGg			2002: 55	0.1	0.3	9.8	6.5	9.0	34.0	Monthly flux = 0 in winter if no measurements are available	1.3	nd [1]
			2003: 130	-2.6	0.0	2.6	1.7	4.8	10.4		0.8	nd [1]
			2004: 120	-1.4	0.1	2.8	1.7	5.7	8.4		0.9	nd [1]
UK-BS	2002-03: TDLAS-EC	Half-hourly	2002: 184 [#]	-296	-7.8	9.5	4.3	19.2	873	TDLAS: Linear interpolation for background	3.69	1.99 [2]
			2003: 141 [#]	-112	-4.6	5.6	1.3	9.0	312	+ cumulative daily flux for peaks	0.68	0.41 [2]
	2004: Manual static chambers & TDLAS	Bi-weekly	2004: 15 [#]	-0.3	0.2	1.4	0.4	0.8	8.9	Static chamber : daily average * 365 days	0.43	0.92 [2]
Ei-CA	Manual static chambers & GC	Weekly + intensive following fertilization	2003: 13 [#]	-7.9	-1.2	0.7	1.0	4.0	4.7	Interpolation between daily means for peaks	0.05	nd [1]
			2004: 43 [#]	-2.0	2.3	12.2	6.0	12.4	77.6	& addition monthly background flux	2.47	0.83 [3]
UK-CPe	Manual static chambers & GC (3 reps / field)	Weekly / monthly + intensive event-based sampling (1 day^{-1})	2002: 51	-3	1	2	2	2	8	Interpolation between daily means for peaks & addition monthly background flux	0.33	nd [1]
			2003: 46	-1	0	1	1	2	5		0.18	nd [1]
			2004: 7	1	1	2	2	3	4		0.39	nd [1]
UK-CPi			2002: 51	1	2	38	4	14	429		3.54	1.19 [3]
			2003: 46	0	0	2	1	2	24		0.48	0.11 [3]
			2004: 7	1	1	1	1	2	2		0.22	nd [1]
Fr-LAe	Manual static chambers & GC (8-10 reps / field)	Bi-weekly during vegetation period (Mar.-Nov.)	2002: 120	-3.1	0	1.2	0	0	14.4	Interpolation between daily mean fluxes	0.17	nd [1]
			2003: 152	-3.1	0	1.1	0	0	26.4		0.17	nd [1]
			2004: 112	-2.6	0	0.2	0	0	3.7		0.03	nd [1]
Fr-LAi	Fast-Box & TDLAS	3 campaigns $N \geq 100$ day^{-1}	2002: 120	-3.3	0	0.7	0	0	14.4		0.56	0.54 [3]
			2003: 152	-2.8	0	4.1	2.1	2.5	140.9		0.80	0.40 [3]
			2004: 112	-1.0	0	0.9	0	0	11.8		0.24	0.13 [3]
Nl-LE	Manual static chambers & PA	Bi-weekly + intensive event-based sampling.	2002: 1898	-12	2	25	5	13	750	Interpolation of fluxes for each cut or fertilizer episode	6.48	3.56 [4]
			2003: 2532	-22	1	13	4	8	350		3.50	1.28 [4]
	ACh & GC-FID-ECD (2 reps)	16 day^{-1}	2004: 1478	-15	0	10	3	12	90		2.20	1.35 [4]
	Fast-Box & TDLAS	2 days * 150 day^{-1}										
Dk-LV1	Manual static chambers & GC-TCD (≥ 4 reps)	1-2 $month^{-1}$	2002: 20	-2.5	0.6	1.4	1.1	1.9	5.6	Interpolation between daily mean fluxes	0.28	0.17 [4]
			2003: 13	-0.8	0.6	3.6	1.7	2.5	21.9		0.64	0.26 [4]
			2004: 6	-0.6	-0.3	0.6	0.3	1.1	1.9		0.08	0.06 [4]
	ACh & GC-TCD (1 rep)	1-2 day^{-1}	2003: 214	-5.3	0.0	1.4	0.8	2.2	16.9		0.3	
			2004: 140	-5.6	0.1	1.9	1.1	2.5	11.7		0.3	
Dk-LV2	Manual static chambers & GC-TCD (4 reps)	1-2 $month^{-1}$	2002: 20	-0.6	0.3	6.1	1.7	4.7	73.1		1.08	0.92 [4]
			2003: 13	-0.6	0.8	2.2	1.4	2.2	8.9		0.47	0.35 [4]
			2004: 6	-0.8	0.3	0.6	0.6	1.1	2.2		0.10	0.05 [4]
CH-OEe	Manual static chambers & PA (2-6 reps / field)	Bi-weekly + intensive event-based sampling	2002: 78	-37	-8	-1	-1	6	27	Interpolation between daily means for peaks (intensive) & addition of the monthly background flux	-0.1	nd [1]
			2003: 198	-54	-8	2	1	9	45		-0.5	nd [1]
			2004: 1496	-65	-4	5	1	8	286		0.2	nd [1]
CH-OEi	ACh & PA (4 reps)	12 day^{-1} rep^{-1}	2002: 169	-36	0	87	13	82	1417	Monthly flux = 0 if no measurements are available	2.6	1.92 [5]
			2003: 463	-40	-6	107	5	94	1529		1.0	0.86 [5]
			2004: 3503	-69	-5	12	2	11	455		1.1	0.59 [5]
It-MA	Diffusion chambers & GC-ECD (8 reps)	Bi-weekly (Jun-Oct.)	2003: 10	0.1	0.1	0.1	0.1	0.1	0.1	Interpolation between flux from chamber & regression vs soil temperature	0.01	0.01 [2]
			2004: 43	0.1	0.1	0.1	0.1	0.1	0.3		0.01	nd [1]
UK-PO	Manual static chambers & TDLAS	1-2 $month^{-1}$	2002: 18	-0.2	0.0	0.7	0.1	0.4	7.9	Daily average * 365 days	0.21	0.41 [2]

ACh: automatic static chambers; EC: Eddy correlation; FID: flame ionization detector; ECD: electron capture detector; TCD: thermal conductivity detector; GC: gas chromatograph; PA: photoacoustic multi-gas analyzer; TDLAS: tunable diode laser absorption spectroscopy; EF: emission factor for direct emissions from added N fertilizer (given as EF_1 in IPCC, 2001b).

[1]EF not determined because there was no fertilizer input.

[#]Daily average fluxes.

[2]EF = 100 × cum. N_2O/(total fertil. × 0.9).

[3]EF = 100 × (cum. N_2O INT − cumcum. N_2O EXT)/(total fertil. × 0.9).

[4]EF = 100 × cum. N_2O/(min. fertil. × 0.9 + org. fertil. × 0.8).

[5]EF = 100 × (cum.N_2O INT − cum. N_2O EXT)/(min. fertil. × 0.9 + org. fertil. × 0.8).

particular: Hu-BG, UK-CP, Fr-LA and CH-OE, though comparisons may also be drawn across sites, following gradients of grazing and fertilization intensity. The study sites were either mown, or grazed, or subject to a combination of both. The somewhat arbitrary classification into "extensive" or "intensive" grasslands (Table 1C) is mainly based on the presence or absence of N fertilizer input, though the density of grazing and the number of cuts per year also co-define management intensity.

2.2. Nitrous oxide flux measurement techniques

Static (non-steady-state) chamber methods (e.g. Skiba et al., 1998) were used at most sites (Table 2). The rate of increase over time in N_2O concentration in the headspace provides a direct estimate of the N_2O exchange flux between the soil and the atmosphere. Nitrous oxide concentrations were determined using either gas chromatography (GC), tunable diode laser (TDLAS) or photo-acoustic (PA) absorption spectroscopy. Trace gas determination was made either on-line in the field with continuous monitors wherever available, or off-line in the laboratory in the case of manual sampling involving PTFE bags, evacuated vials or syringes. In the case of static chamber measurements made at CH-OE, where headspace N_2O concentration was determined once per minute using a photo-acoustic analyzer with a noise of 20 ppb N_2O, and where fluxes were determined from the linear regression slope of concentration *versus* time over a 10-min interval, the estimated flux detection limit was 10 ng N_2O-N m^{-2} s^{-1} (Flechard et al., 2005).

Manual chamber measurements (MCh) were typically carried out at bi-weekly intervals during the growing season, with, at some sites, additional and intensified measurement campaigns when higher N_2O emissions were expected to occur, for example, following the application of fertilizer. Automated chambers (ACh) were also tested and implemented at three sites (Nl-LE, CH-OE, Dk-LV), providing a higher time resolution. Soil pore space N_2O concentrations were in addition monitored at CH-OE during the whole project (Flechard et al., 2005). Other methods used to better characterize spatial and temporal variability were investigated by TDLAS-Eddy Covariance (Di Marco et al., 2004; Leahy et al., 2004) at UK-BS, and TDLAS-Fast-Box measurements (Hensen et al., 2006) at Nl-LE and Fr-LA. Unlike conventional static chamber measurements, in which the headspace remains closed over vegetation for typically 10 min up to several hours, the fast response (>1 Hz) of the TDLAS allows a quick (e.g. 20 s) determination of the N_2O concentration increase within the chamber. This not only minimizes the ecosystem disturbance generated by a

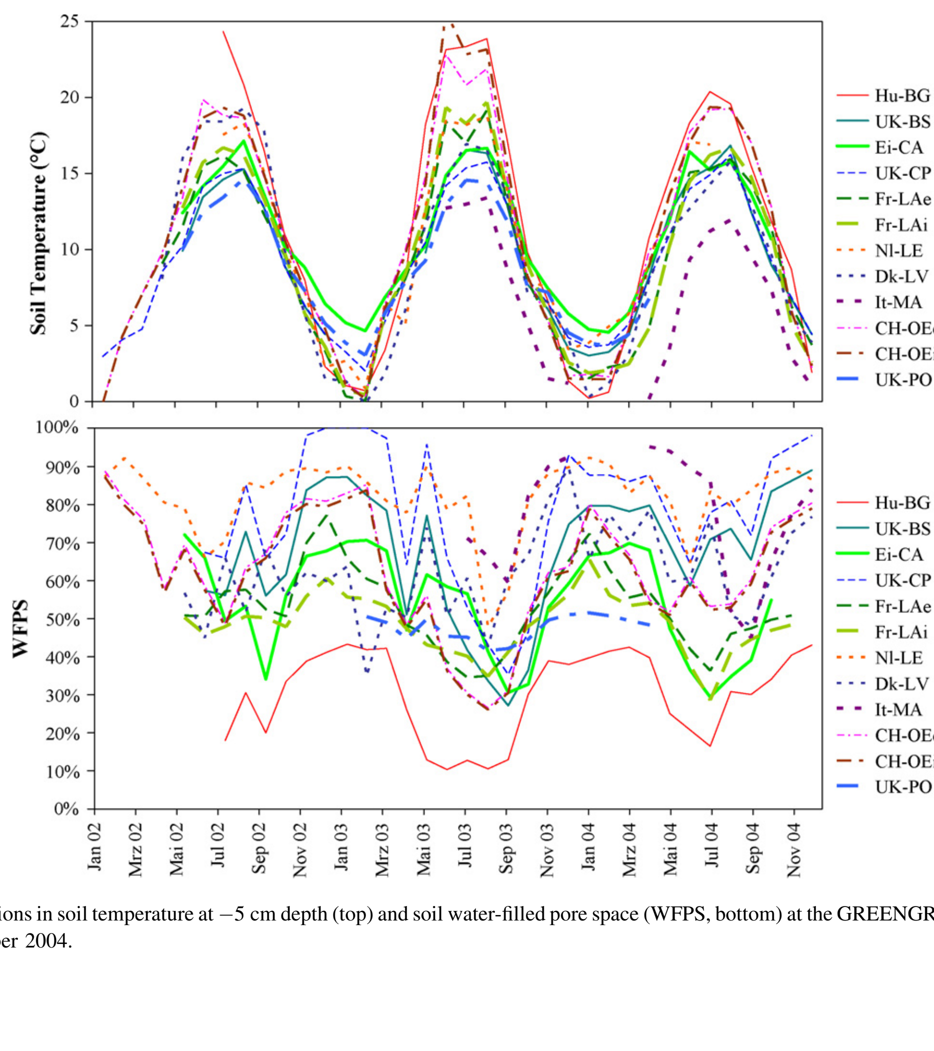

Fig. 1. Monthly variations in soil temperature at −5 cm depth (top) and soil water-filled pore space (WFPS, bottom) at the GREENGRASS sites for the interval spring 2002—December 2004.

prolonged chamber closure, but also maximizes the potential number of chamber measurements that one can carry out during a given time frame (up to 150 per day).

To provide annual emission estimates, various integration methods were implemented, depending on the site-specific sampling strategies (Table 2). While TDLAS-EC provided continuous, field-scale measurements of the soil-atmosphere N_2O exchange at UK-BS, many other sites had to rely on periodic (bi-weekly) or episodic chamber measurements that were not continuous in either space nor time. In the latter case caution must be exerted to avoid systematic over- or under-estimation that may arise as a consequence of potentially biased flux sampling. At some GREENGRASS sites (e.g. Flechard et al., 2005), the flux dataset was divided into "peak events" and "background", so that the high emission values observed during peaks are not over-represented in the annual cumulative estimate. Although the arithmetic mean of a flux dataset in theory provides an effective integration over space and time, peak fluxes may in practice be over-represented in time because manual measurements tend to be concentrated around periods of intense N_2O activity, e.g. following the application of fertilizer. An integration bias is then likely to occur if the arithmetic mean of a skewed distribution is applied to the whole year, when in fact on most days of the year, in so-called background conditions, the N_2O flux hardly differs from zero, and when the bulk of the annual emission occurs within a few peak days.

Soil temperature and soil water content (SWC), from which the WFPS fraction was derived, were continuously monitored at most sites (Fig. 1), as were air temperature, solar radiation, precipitation and wind speed. At sites where SWC was not measured continuously through the entire monitoring period, either data from an adjacent field site were used (Dk-LV, UK-CP), or SWC was simulated (Nl-LE, July 2002–May 2003) with a simple model of evapo-transpiration (P. Calanca, pers. com.), based on standard meteorological data and soil hydrological properties and calibrated using measured data from the site.

3. Results and discussion

3.1. Spatial and temporal variability of N_2O fluxes

Measured instantaneous N_2O fluxes were extremely variable in time, in space at each site, and also from site to site, depending on weather and management practices. Overall across sites they ranged from -300 to $+1500$ ng N_2O-N m^{-2} s^{-1}, but the bulk of the distribution, between the 25th to the 75th percentiles, was found in a narrow range from -10 to $+20$ ng N_2O-N m^{-2} s^{-1} (Table 2). Here, a plus "+" sign indicates emission to the atmosphere, while minus "−" indicates an uptake by soil. Annual median fluxes at each site were mostly in the range 0 to $+10$ ng N_2O-N m^{-2} s^{-1}, while average values were generally a factor of 2–10 higher than the median, denoting skewed datasets. Frequency distributions of measured fluxes tended to be quasi-lognormal (except for the presence of negative values) at fertilized sites with higher N inputs (UK-BS, UK-CPi, Fr-LAi, Nl-LE, CH-OEi), whereas flux data were more normally distributed at unfertilized or semi-natural sites (Hu-BG, UK-CPe, It-MA, CH-OEe). The highest instantaneous emission fluxes, in excess of $+100$ ng N_2O-N m^{-2} s^{-1}, were measured at UK-BS, UK-CPi, Fr-LAi, Nl-LE, CH-OEi, which were all intensively managed systems. Occasional short-term negative (deposition) fluxes were detected at almost all sites. The highest instantaneous uptake rates were measured by TDLAS-EC at UK-BS (Table 2), where downward fluxes were observed 43% of the time. More than half of them were rejected after a post-processing stationarity filter, derived from Foken and Wichura (1996), was applied, but in the final dataset there remained 19% uptake fluxes which could not be discarded for any obvious reason. It was unclear whether the remaining high uptake rates may have resulted from measurement artefacts, such as sudden changes in TDL cell pressure, rather than from actual soil processes (Di Marco, 2005), but it was decided not to discard those in order to avoid introducing a statistical bias in the annual budget. Significant negative fluxes were also consistently measured at CH-OE, especially on the unfertilized field (CH-OEe), simultaneously with sub-ambient N_2O concentrations in the soil, indicative of a consumption process which is active in dry as well as in wet conditions (Flechard et al., 2005).

The fast box technique was especially significant for the assessment of spatial variability in N_2O fluxes on both extensive (Fr-LAe) and intensive (Fr-LAi) fields at the French site, and also at Nl-LE. These sites were all grazed by cattle. During two measurement campaigns in September 2002 and June 2003 at Fr-LAi, the coefficient of variation (CV) of measured fluxes was 385% and 246% ($N = 144$ and $N = 100$, respectively). Even on the unfertilized field Fr-LAe in June 2003, a CV of 370% ($N = 100$) was found, though the magnitude of N_2O fluxes here was less than on Fr-LAi. At Nl-LE, a similar picture was found, with N_2O fluxes varying from -100 ng N_2O-N_2O-N m^{-2} s^{-1} to + 800 ng N_2O-N m^{-2} s^{-1} on one given day within a 25 m × 10 m area of the grassland site (Fig. 2). It was concluded that at least 30 sampling points randomly distributed across the whole field are required to obtain a reliable field-scale estimate of the flux.

Semi-continuous, field-scale TDLAS-EC measurements made at UK-BS from June 2002 to June 2003, a total of 4000 measurement hours, showed the high temporal variability of emissions. For example, under conditions in June 2002 that were optimal for N_2O production, the N_2O response to fertilization was very fast, peaking within 1 h of application at 2.5 mg N_2O-N m^{-2} s^{-1}. Daily fluxes averaged about 300 ng N_2O-N m^{-2} s^{-1} over the 4 days following this fertiliser application (Di Marco et al., 2004; Di Marco, 2005). This fast response would be difficult to measure by conventional methodology, namely manually operated static chambers, and may lead to an underestimation of the total flux. By contrast, at the fertilized but non-grazed grassland of

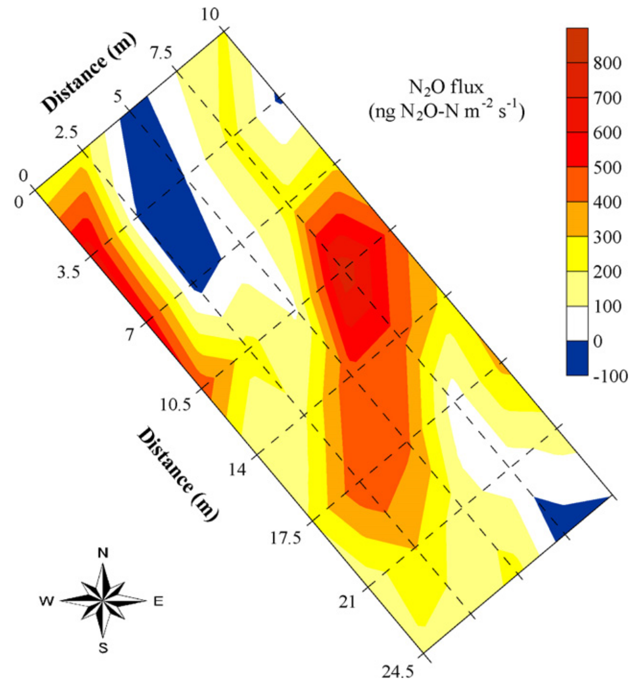

Fig. 2. Spatial variability of N_2O fluxes measured with the Fast-Box technique at Nl-LE. The contour plot is based on flux measurements at 40 points on the 25 m × 10 m grid, each sampling point being at the corner of a 2.5 m × 3.5 m rectangle.

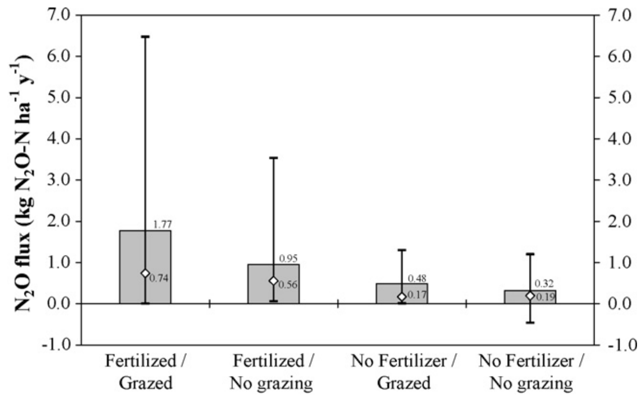

Fig. 3. Mean annual N_2O emissions at the GREENGRASS sites and effect of fertilization and grazing. Greyed columns are arithmetic mean annual fluxes, diamonds are median values, across all sites, for the years 2002–2004. Vertical bars show the full range of annual fluxes.

Dk-LV1, where seasonal variability was investigated using both discontinuous MCh and one ACh, the coefficient of variations were similar for both measurement systems, with 130–180% for MCh data and 160–180% for ACh data, in spite of the large difference in sample number (Table 2). In showing such temporal as well as spatial homogeneity, however, the intensively managed Dk-LV1 site was the exception rather than the rule among the fertilized sites, but the absence of grazing, in comparison to Fr-LA or Nl-LE, may have contributed to the reduced variability.

While spatial and temporal heterogeneity in N_2O fluxes from intensive grasslands plead for equally intensive measurement efforts using EC or at least ACh, the data from the non-fertilized sites of GREENGRASS suggest that the use of simple, low-cost static chambers is justified over extensive systems, in order for instance to include more treatments or measurements at remote locations. Uncertainties in annual N_2O emission estimates from manual chambers remain high; at CH-OEi for example, where emission peaks were extremely steep and short-lived, the asymmetrical uncertainty range for the cumulative flux over 2.5 years of 4.7 kg N_2O-N ha^{-1} was estimated to be $\begin{pmatrix}+2.6\\-1.3\end{pmatrix}$ kg N_2O-N ha^{-1}, i.e. up to 50% (Flechard et al., 2005).

3.2. Annual fluxes and emission factors

The highest annual emission by far occurred at Nl-LE in 2002 (+6.5 kg N_2O-N ha^{-1} year^{-1}), and, at the other end of the scale, the extensively managed field at CH-OEe proved to be a net sink for N_2O in 2002 and 2003 (Table 2). There was substantial inter-annual variability, but at most fertilized sites the highest N_2O emissions per unit N applied were observed in 2002. Unsurprisingly, intensively managed systems were clearly stronger sources of N_2O than extensive grasslands. Annual emissions above 2 kg N_2O-N ha^{-1} year^{-1} all occurred at sites with annual fertilizer inputs above 150 kg N ha^{-1} (UK-BS, UK-CPi, Nl-LE, CH-OEi), though there were also sites where high N inputs did not systematically trigger large emissions (Fr-LAi, Dk-LV1).

Mean annual N_2O fluxes are shown in Fig. 3, where data from all GREENGRASS sites and from the three measurement years were pooled into fertilized/unfertilized and grazed/ungrazed systems. Grazing appeared to enhance N_2O emissions, which may be interpreted as a consequence of both the maintained presence of active hotspots of N_2O production via a continuous supply of animal urine and dung, and of the trampling effect that increases soil compaction (Oenema et al., 1997). The grazing effect, however, was observed primarily at fertilized sites and was by no means systematic. At the semi-arid, semi-natural site of Hu-BG for example, the observed average N_2O flux was only 10% higher at Hu-BGg (grazed) than at Hu-BGc (control), and taking into account the bulk error of sampling and analysis, this difference is not significant. This lack of a clear and systematic response of N_2O emissions to grazing may partly originate in sampling biases and methodological difficulties associated with chamber measurements over grazed terrain. At some sites, and at least part of the time, chambers were fenced off to prevent damage by animals; although this did not necessarily reduce the input of urine and dung, the effect of trampling was absent. Further, the proportion of all chamber measurements that were made directly over urine patches or cow pats may have been lower than the fraction of the field area actually covered by animal excreta, first of all because this is extremely difficult to estimate, but perhaps also out of concern that the overall flux might otherwise be over-estimated. In addition, the large differences observed in Fig. 3 between arithmetic mean and median annual fluxes suggest that the large difference between ‘‘grazed’’ and ‘‘no grazing’’ in the ‘‘fertilized’’ case may simply result from a few outliers such as Nl-LE (see also Table 2). No overall relationship was found between N_2O emissions and the C/N ratio of soils, but the range of C/N values across the sites investigated (9.4–14.1; Table 1B) was probably too narrow to derive any meaningful relationship, unlike for example in studies over forested histosols (Klemedtsson et al., 2005).

Annual emission factors for emissions from N inputs, known as ‘‘EF_1’’ in the IPCC Guidelines Tier 1 (IPCC, 2001b), are also simply referred to as ‘‘EF’’ in this paper, since the other EFs of the IPCC methodology (EF_2–EF_6) are not studied here. Calculations of the annual EF (Table 2) were, wherever possible (UK-CP, Fr-LA, CH-OE), made by subtracting the N_2O flux of the unfertilized treatment from that of the fertilized field, before dividing by the fertilizer input, which was adjusted for the volatilization as NH_3/NO_X (assumed to be 10% for mineral and 20% for organic fertilizers; IPCC, 2001b). The assumption in such differential treatments was that the difference between both fields of biological N_2-fixation and of crop residue mineralization was negligible, though the data from CH-OE may suggest otherwise (Flechard et al., 2005; Ammann et al., 2007). In cases where there was no unfertilized treatment or control (UK-BS, Nl-LE, Dk-LV, UK-PO), no correction was made for background fluxes, which makes inter-comparisons between sites more difficult. Annual EF values ranged from 0.01% to 3.56% (Table 2), with an arithmetic mean value of 0.72% and a median of 0.41% (Table 2).

Alternatively, a scatter plot of annual N_2O fluxes *versus* adjusted annual N fertilizer inputs across all sites (Fig. 4) may be interpreted using linear regressions for the years 2002–2004. The regression slopes (expressed in percentage terms) provide estimates of mean Europe-wide EFs from added fertilizers in grasslands, and the intercepts mean annual background emissions (Bouwman, 1996; Helgason et al., 2005). The N input through cattle urine and droppings during field grazing is in this graph not considered alongside fertilizer as a source of available N for soil N_2O production in the calculation of EF_1. Whether field-produced excreta effectively result in an additional N input, or simply in an enhanced turnover of grassland organic matter, remains a matter for discussion and a question of definition. The IPCC Guidelines consider N_2O emissions from field droppings by grazing cattle quite separately under the topic ‘‘N_2O emissions from manure management’’, with a separate emission factor EF_3 of 2% of the excreted N (IPCC, 2001b). Thus the fraction of N_2O emissions directly attributable to on-field urine and cattle droppings should theoretically be subtracted from the total (measured) N_2O emission fluxes, in order for the observation-based EF_1 and the IPCC's recommended EF_1 values to be mutually consistent. However, since the N inputs involved and the default EF_3 value of 2% are highly uncertain, and given the existing large scatter in Fig. 4, no such correction was made, and the observation-based EF_1 values thus represent upper limits of the true EF_1. The merit of Fig. 4, nonetheless, consists in showing the potentially high inter-annual variability in emission factors. While for 2002 the regression yields a slope of 0.0146 ± 0.01, i.e. EF = $1.46 \pm 1.0\%$, which is not significantly different from the IPCC default value of $1.25 \pm 1\%$, in 2003 and 2004 the EF were a factor 3 lower ($\sim$0.5%). The overall EF for the whole experiment derived from Fig. 4 is 0.75%, as compared with the arithmetic mean of 0.72% calculated from all annual EFs of the individual sites (Table 2). Background emissions inferred from the regression *y*-intercepts (no added fertilizer) were in the range 0.15–0.3 kg N_2O-N ha^{-1} $year^{-1}$ (overall mean: 0.28 kg N ha^{-1} $year^{-1}$), well below the default value of 1 kg N ha^{-1} $year^{-1}$ recommended by Bouwman (1996) to the IPCC, but more in keeping with the value of 0.405 kg N ha^{-1} $year^{-1}$ obtained by Helgason et al. (2005) using a similar type of regression for a wide range of Canadian agroecosystems. At most sites, 2002 was a wetter-than-average year, whereas during the summer of 2003 a severe drought prevailed (Fig. 1), with the likely consequences that the major soil sources of N_2O, namely nitrification and denitrification (Smith et al., 2003), being most active in the WFPS range 50-80% (Davidson, 1991), were overall stimulated in 2002, but suppressed in 2003.

Higher EFs in 2002 might incidentally also be partly a consequence of recent field history at sites such as Ei-CA and CH-OE, where grassland was established only in 2001. At CH-OE, the conversion of an 8-year ley-arable rotation to permanent grassland involved ploughing up the field in November 2000, which may have enhanced the mineralization of soil organic matter, as compared with older grasslands such as Hu-BG, UK-BS or Fr-LA. The effect

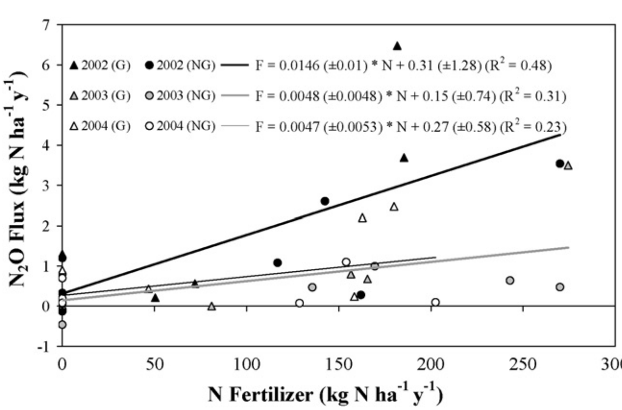

Fig. 4. Determination of mean annual emission factors (regression slopes) and background emissions (regression intercepts) across all GREENGRASS sites. Triangles represent cumulative annual N_2O fluxes at sites with grazing (G), circles represent non-grazed (NG) sites. Annual fertilizer inputs are adjusted for NH_x/NO_x losses (10% for synthetic fertilizers, 20% for manures and slurries), according to IPCC guidelines (IPCC, 2001b). Ninety-five percent confidence intervals for regression parameters are indicated within brackets.

of conversion on the availability of soil mineral N may still have been felt in 2002, though no data are available to substantiate this hypothesis.

3.3. Empirical modelling of N_2O emission factors for grasslands

Annual differences in EFs suggest that climatic variability significantly affects the N_2O source strength of grassland ecosystems from year to year, and this should be taken into account in emission inventory methodologies (Flynn et al., 2005; Roelandt et al., 2005). In Fig. 4, background emissions and EFs were given at annual time scales. Such data conceal the seasonal variability in N_2O exchange that arises from variations in important macro-drivers of N_2O evolution such as soil temperature, SWC (or WFPS), rainfall, and livestock grazing density (GD). The comparison of annual EFs at individual sites (Table 2), or of Europe-wide EFs (Fig. 4), between the three years of the GREENGRASS experiment, allows one to speculate qualitatively on the reasons for the observed differences, but a quantitative analysis and N_2O flux prediction on the basis of annually averaged N_2O macro-drivers is precluded because variations are damped out.

Thus, in the following analysis the annual cumulative N_2O flux data are split into "events" of shorter time spans (Appendices A and B). An event may be defined by an episode of intense N_2O emission following one fertilizer application, or by a growth phase, or by any time interval from a few days up to a few weeks during which conditions of soil temperature and moisture, and of grazing, vegetation and weather, can be considered sufficiently homogeneous. For fertilized sites, events were delimited in time by an observation of the N_2O time series following the application of fertilizer; the end of the event is defined either as the day before the next fertilizer application, or as the date when the N_2O flux reverts to a background level (Flechard et al., 2005). The event-cumulative N_2O flux is thus attributed and normalized to the previous fertilizer input. Dobbie and Smith (2003) used a similar approach in their analysis of the relationship between rainfall and N_2O emission. To obtain a meaningful correlation, they chose time intervals of 4 weeks starting shortly before and following fertilizer application. The present objective is likewise to derive an empirical regression model from GREENGRASS event-resolved data, to predict likely values of EF (or range thereof) depending on the prevailing weather, soil and management conditions, at a typically monthly time scale. The observation by Dobbie and Smith (2003) that, on average, 77% of the annual N_2O flux from grassland cut for conservation is emitted within 4 weeks of fertilizer application supports our use and definition of event-based emission factors.

The objective here is however not to simulate instantaneous N_2O fluxes *per se*, which would, in addition to soil temperature and moisture, require a knowledge of soil available N and C (Conen et al., 2000). While measurements of soil concentrations of NH_4^+ and NO_3^- were made periodically at some GREENGRASS sites (Appendices A and B), no overall correlation was found between instantaneous nor cumulative N_2O fluxes and soil mineral N availability, not least because soil available N sampling was infrequent and not necessarily carried out on days of high N_2O emission.

3.3.1. Parameterization of background N_2O fluxes

Measured, event-based cumulative background N_2O fluxes (F_{bgnd}) were normalized to a common monthly time scale in order to remove the effect of the different integration times (Appendix A). Normalized N_2O fluxes (Appendix A) were positively correlated with soil temperature (Eq. (1), $R^2 = 0.19$, $P < 0.001$), but no correlation was found with soil WFPS nor with the stocking density. There was incidentally no visible correlation either between annual background N_2O emissions by grasslands and total atmospheric, reduced and oxidized N deposition as calculated by the EMEP model (Table 1C; EMEP, 2003), though this link has been made previously for non-fertilized systems (Skiba et al., 1998). Background fluxes tended to increase with temperature, with a clear tendency for uptake (negative) fluxes (black symbols) to occur at temperatures below 10 °C, which tended to coincide with high WFPS values, typical of autumn/winter conditions (Fig. 5).

$$F_{bgnd} = 13.1\,(\pm 5.8) \times T_{soil} - 79.3\,(\pm 71.2) \qquad (1)$$

where F_{bgnd} has units of g N_2O-N ha^{-1} $month^{-1}$, T_{soil} is soil temperature in °C, and brackets indicate the 95% confidence intervals of the regression parameters.

Fig. 5 illustrates the difficulty of analyzing the separate effects of soil temperature and SWC on N_2O fluxes, since these two variables show a strong negative correlation over seasonal time scales. It may be that the uptake fluxes observed at low soil temperatures are more connected mechanistically to the high SWC than to temperature itself, since the reduced O_2 availability and entrapment of N_2O in wet soils leads to a

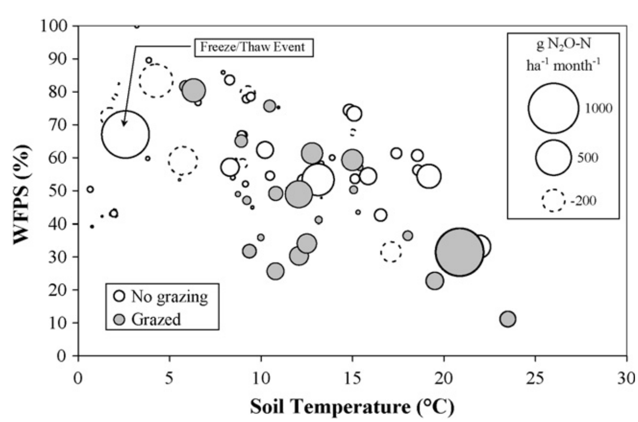

Fig. 5. Influence of soil temperature and soil water-filled pore space (WFPS) on monthly rates of "background" N_2O exchange for the GREENGRASS sites. Bubble areas are proportional to the N_2O flux values, which are normalized and expressed as g N_2O-N ha^{-1} $month^{-1}$. Dashed bubble outlines denote negative fluxes, i.e. N_2O uptake.

consumption of N_2O and a reduction to N_2 through complete denitrification (Davidson, 1991; Clough et al., 2005). Uptake fluxes were however also observed at lower WFPS levels in summer conditions at CH-OE (Flechard et al., 2005), though the mechanism for this is unknown. Eq. (1) provides the simple framework in this study for predicting background N_2O fluxes as a function of soil temperature, but a lot of the variability in observed F_{bgnd} remains unexplained. In particular, the monthly N_2O emissions in August 2002 at Hu-BG, events labelled "Hu-BGc-Sum1" and "Hu-BGg-Sum1" (Appendix A), reached levels of almost 1 kg N_2O-N ha^{-1} $month^{-1}$, although soil WFPS was only 31% and there was no fertilizer added. Likewise, the freeze-thaw event at CH-OE in March 2004, labelled "CH-OEi-Win1" (Appendix A, Fig. 5), contributed an emission of 0.21 kg N_2O-N ha^{-1} over 7 days, equivalent to 0.9 kg N_2O-N ha^{-1} $month^{-1}$. This last event, resulting from the alternate effects of soil freezing and thawing at the end of winter (Goodroad and Keeney, 1984), was considered a special case and thus was the only event not to be included in the overall regression of F_{bgnd} *versus* soil *T*. The diurnal effect of soil temperature on N_2O solubility in water and on its partitioning between the aqueous and gaseous phases in the soil (Blackmer et al., 1982) is likely to have contributed to the observed variations in source/sink strength, but the magnitude of this effect cannot be estimated on the basis of monthly data.

3.3.2. Parameterization of emission factors from added fertilizer

In a first step, observation-based EFs were calculated from individual fertilization events (Appendix B), as the difference between measured F_{N_2O} and F_{bgnd}, divided by the event fertilizer input N_{fert}, adjusted for NH_x/NO_x volatilization losses, such that:

$$\mathrm{EF}(\%) = 100 \times \frac{F_{N_2O,meas} - F_{bgnd}}{kN_{fert}} \quad (2)$$

where *k* is 0.9 for synthetic, or 0.8 for organic, fertilizer (IPCC, 2001b). At sites with differential intensive/extensive treatments (UK-CP, Fr-LA, CH-OE), the value of F_{bgnd} used in Eq. (2) was the flux measured over the extensive grassland in parallel to the fertilization event of the intensive field. If no such data were available, a regression of F_{bgnd} *versus* soil temperature was used to determine the relevant background level, as shown in Eq. (1). The event-based EFs resulting from Eq. (2) were then analyzed for correlations with soil temperature, SWC, rainfall and grazing intensity. Emission factors increased with soil temperature (Fig. 6), and whilst grazing seemed to have a positive though marginal effect on EF, the relationship to WFPS was less straightforward. Although there were exceptions and the variability was high, EFs seemed to peak in the WFPS range 65–85%. This is consistent with the concept (Davidson, 1991) that N_2O evolution from soils, resulting from the combined source strengths of nitrification and denitrification, but also from N_2O consumption processes in water-logged soils, is only significant within a limited range of WFPS. To parameterize this relationship, we define here a bell membership function *B*(WFPS) such that:

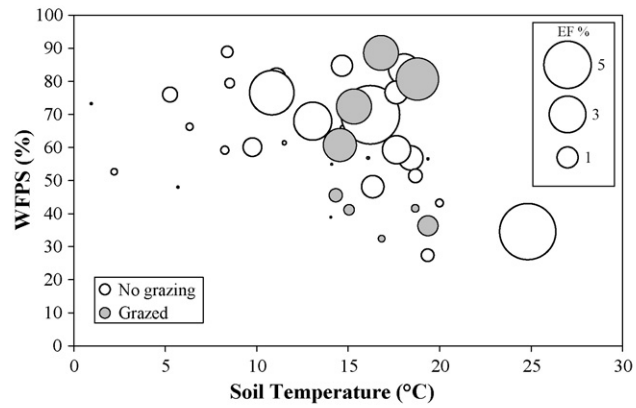

Fig. 6. Influence of soil temperature and soil water-filled pore space (WFPS) on measured emission factors (EF) from fertilizer application. Each bubble describes one "event" or episode as defined in the text. Bubble areas are proportional to the EF value.

$$B(\mathrm{WFPS}) = \frac{1}{1 + (\mathrm{WFPS} - (c/a))^{2b}} \quad (3)$$

where WFPS is expressed in % from 0 to 100, the centre of the bell is *c* = 75%, and *a* = 15% and *b* = 3. In fuzzy logic, B describes the "degree of membership" to a WFPS range where conditions are optimum for N_2O emission. Thus B varies from 0 in very dry conditions (WFPS < 40%), to a maximum value of 1 in the WFPS range 70–80%, and down again to 0.04 for WFPS = 100%. The values of the parameters *a*, *b* and *c* were obtained by maximizing the coefficient of determination (R^2) of the regression between EF and *B*. The optimum level of WFPS for N_2O evolution at *c* = 75% is somewhat higher than, though not inconsistent with, the value of about 65% suggested by Davidson (1991).

The last step in the parameterization of EF was the multiple linear regression of ln(EF) *versus* soil *T*, *B*(WFPS), cumulative rainfall (P) and grazing density (GD). This confirmed the positive effects of *T*, *B* and *P* on EF (Eq. (4)), but no significant correlation was found between EF and GD on an event basis, even though on an annual basis grazed sites had been shown to be higher N_2O emitters than non-grazed sites (Fig. 3). The regression *versus T, B* and *P* explains half of the variability ($R^2 = 0.48$) in the observed ln(EF) across the $N = 40$ fertilization events included in the dataset (Appendix B):

$$\ln(\mathrm{EF}\%) = -5.52(\pm 1.75) + 0.18(\pm 0.10) \times \text{soil } T + 2.40(\pm 1.21) \times B(\mathrm{WFPS}) + 0.01(\pm 0.01) \times P \quad (4)$$

with soil *T* expressed in °C, *B* as in Eq. (3), and *P* is the event cumulative rainfall normalized to a monthly time scale (mm $month^{-1}$).

The exponential response of EFs to temperature and the bell-shaped response to soil moisture are in evidence in Fig. 7,

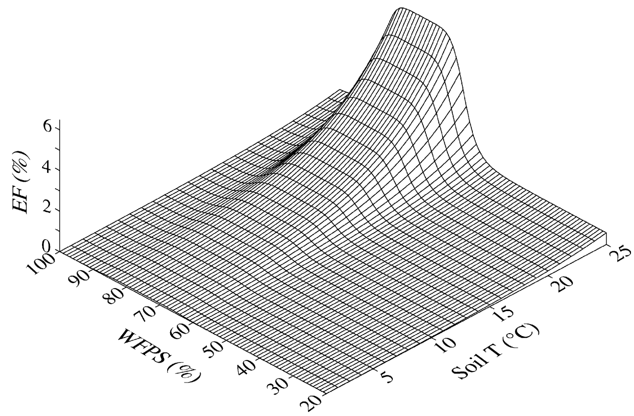

Fig. 7. Fitted response of the emission factor (EF) from fertilizer to soil temperature and WFPS, assuming a monthly rainfall of 50 mm (after Eq. (4)).

which shows a simulation of the EF, assuming a rainfall of 50 mm during the month following fertilizer application. Fractional losses of N_2O-N up to 6.5% of applied fertilizer N are predicted for a soil temperature of 25 °C and WFPS between 70% and 80%. In practice, such warm and wet conditions seldom occur simultaneously in European grasslands because soil temperature and wetness tend to be inversely correlated (Figs. 5 and 6), and EFs are more likely to be of the order of 0.1–3% (Appendix B). The exceptionally high EF value of 7.6% at Nl-LE for the event "Nl-LE-Sum1A" in 2002 (Appendix B) coincided with a near-optimum WFPS level of 70%, and despite a moderate soil temperature (16.2 °C). By contrast, the high EF of 7.1% obtained at CH-OE during the dry summer of 2003 ("CH-OEi-AN3"), occurring at a WFPS level of 35% (Appendix B; Fig. 6), was rather unexpected even though the mean soil temperature was very high at 24.8 °C. Here it may be surmised that the WFPS fraction at a depth of −5 cm was not in this case an adequate scaling factor for the N_2O source strength, because the N_2O production and emission took place on the soil surface, after the scattered AN pellets were humidified by moderate rainfall that did not significantly affect the WFPS status of the topsoil. In fact, the topsoil layer most relevant for N_2O production and exchange with the atmosphere is much shallower than the depth at which temperature and moisture are generally monitored in many field studies (typically 5–10 cm). This is because the scale length of N_2O in soil is of the order of 0.7–2.8 cm (Neftel et al., 2000), which means that N_2O produced at greater depths is unlikely to reach the soil surface and the atmosphere before being consumed in soil microbial processes. Thus, although the regression parameter for P in Eq. (4) is barely significant at 95% (0.01 ± 0.01), it is important to include precipitation as a predictor of EF for cases when WFPS is low and N_2O emission can nonetheless be high owing to surface processes.

No distinction was made in the empirical determination of EF between the different types of fertilizer, whether organic (e.g. cattle slurry, farmyard manure) or mineral (e.g. AN, CAN, AS, NPK), because this would reduce the number of points available for the overall regression across sites and thus the reliability and stability of the model predictions. Differences between fertilizer types have been well documented (FAO/IFA, 2001), and the influence of N fertilizer form on N_2O production was specifically studied within GREENGRASS at the UK-CP site (Jones et al., 2007). Such datasets could be used to scale a generic form of the relationship presented in Eq. (4).

3.3.3. Climate-induced variability in N_2O emission factors

In establishing empirical relationships between observed N_2O fluxes and soil, meteorological and management conditions, the modelling approach presented here can be compared to that of Skiba et al. (1998), who simulated hourly rates of N_2O emission on the basis of overriding relationships to soil temperature, moisture and annual N input for a wide range of Scottish soils and vegetation types. Similarly, a recent compilation and statistical (Principal Components Analysis) evaluation of mainly European and North American datasets of N_2O fluxes over croplands and grasslands yielded two empirical models that predict annual N_2O emissions on the basis of spring temperature and summer precipitation for crops, and on the basis of annual fertilizer N input and winter temperature for grass (Roelandt et al., 2005).

In the present paper the emphasis is on the explicit determination and modelling of the seasonal and inter-annual variations in N_2O *emission factors* rather than fluxes. The EF approach is based on the assumption that cumulative N_2O emission is a linear function of N input over the same time interval (Fig. 4), or in other words, that the emission factor is independent of added N, though this view has been challenged (McSwiney and Robertson, 2005). In this context, as within the framework adopted by the IPCC for estimating national emission inventories, the amount of fertilizer N input is simply used as a scaling factor, but the variability in emission factors should be quantified and accounted for (Flynn et al., 2005).

The European climate gradient in GREENGRASS sites, as well as changing meteorological conditions from year to year, has provided ample evidence that meteorology/climate influence emission factors. The highest EFs were consistently measured in the Netherlands (Nl-LE) and in Scotland (UK-BS). These sites are not necessarily the wettest in terms of annual precipitation (only 780 mm and 638 mm, respectively; Table 1A), but in terms of WFPS these soils are systematically wetter throughout the year than most other sites (Fig. 1). Critically, however, their WFPS level mostly remains below saturation, in the optimum range for N_2O emissions of 60–90%. By contrast, Fr-LA has an organic soil with a high total porosity (0.76 m^3 m^{-3}) and a low bulk density (0.64 kg l^{-1}), and as a result the WFPS level rarely exceeds 50–60% during the growing season when fertilizer is applied (Table 1A). Consequently the EFs observed at Fr-LA were low, typically less than 0.5% (Table 2), even though this site has the highest annual precipitation among the GREENGRASS sites with

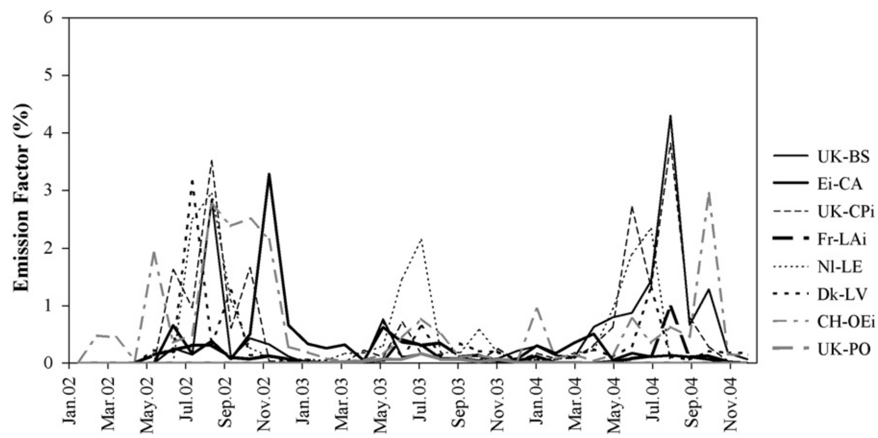

Fig. 8. Simulated seasonal and interannual variability in emission factors (EF) from added N fertilizer, within the time frame of the GREENGRASS project (after Eq. (4)).

1313 mm. The GREENGRASS data are broadly consistent with the analysis by Dobbie and Smith (2003), who describe a linear relationship of annual EFs for a range of grassland sites in Great Britain to WFPS in the range 60–85%. In the present case, the functional relationship of EF is to B(WFPS) rather than to WFPS itself (Eqs. (3) and (4)), in order to cover the whole humidity range and avoid an over-estimation of EF at water saturation (WFPS = 100%), when little or no N_2O emission is expected (Davidson, 1991).

The 2003 heat wave and severe drought over large regions of Europe provided an insight into potential changes in emission factors for N_2O as a response to climate change. The reduction in EFs across the GREENGRASS sites during the summer 2003 resulted from the reduction in WFPS, itself a consequence of reduced precipitation. The higher soil temperature had a marginal effect only at sites where soil moisture was not limiting. Significant emissions were nonetheless occasionally observed in very dry conditions, at WFPS below 40% (e.g. CH-OE, Hu-BG), which in some cases may be attributed to the effect of precipitation and processes occurring on the surface of a warm soil. A wide range of potential EFs could have been expected at the fertilized GREENGRASS sites for 2002–2004 on the basis on the empirical relationships to monthly mean temperature, WFPS and rainfall defined by Eq. (4) (Fig. 8). Seasonal as well as inter-annual variations are large, though the concept of an emission factor from applied fertilizer only makes sense during those months when fertilizer is likely to be applied, i.e. mainly during the growing season. This simulation shows the advantage of using monthly, or at least seasonal, EFs that are applied to fertilizer inputs over the same time interval, as opposed to an annual EF approach. The link between EF and soil and environmental drivers of N_2O emission, albeit empirically based, makes it possible to single out 2003 as a "low emission" year, and 2002 as having a potential for higher emissions than the average. Quite apart from the fact that the mean overall EF of the GREENGRASS sites for the whole experiment (0.75%) was substantially lower than the IPCC default EF of 1.25%, the current IPCC methodology cannot address climate-induced variability in N_2O emissions, an issue that should become a priority for future N_2O research (Roelandt et al., 2005) and addressed in a future revision of the IPCC methodology.

4. Conclusion

Nitrous oxide flux monitoring from grassland sites within GREENGRASS has shown that significant progress has been made in measuring N_2O fluxes at the field and annual scales, using state-of-the-art technologies such as TDL eddy correlation and fast-box measurements. The need for continuous data series (automatic chambers), as opposed to manual, intermittent measurements, has been emphasized, especially over fertilized and grazed sites where temporal variability is highest. Emission factors from nitrogen input were highly variable from site to site and from year to year, but readily available parameters such as soil temperature and moisture explain half of that variability when studied at time scales of the order of a month or a season. Despite the considerable remaining uncertainty in both measurements and in our understanding of processes that regulate N_2O emissions, this research supports previous publications that argue for, and offer models for, climate-sensitive emission factors for N_2O instead of the current IPCC default value. This is required, not only to improve current estimates of N_2O emissions but also to predict the variations in future emissions in response to climate change.

Acknowledgements

This work was carried out in the framework of, and largely funded by, the European Union project GREENGRASS (EVK2-2001-00105), and contributes to the COST Action 627. Additional funding by the various national governments is gratefully acknowledged. We are thankful to Franz Conen for his comments on the article.

Appendix A. Breakdown of annual cumulative N_2O fluxes: background fluxes

Site-event	Date		Duration (days)	Soil T[a] (°C)	WFPS[a] (%)	Rain (mm)	GD (LSU ha^{-1})	Soil min. N (mg N kg^{-1})	N_2O flux (meas.) (g N ha^{-1} month^{-1})	N_2O flux (fit.)[b] (g N ha^{-1} month^{-1})
	Start	End								
Hu-BGc-Sum1	1 August 2002	31 August 2002	30	20.9	31	59	0.0	nd	937	193
Hu-BGc-Aut1	1 September 2002	30 November 2002	90	12.1	30	123	0.0	7.5	99	79
Hu-BGc-Win1	1 December 2002	28 February 2003	89	1.3	42	105	0.0	nd	−1	−62
Hu-BGc-Spr1	1 March 2003	31 May 2003	91	10.8	26	64	0.0	16.7	107	62
Hu-BGc-Sum2	1 June 2003	31 August 2003	91	23.5	11	77	0.0	nd	99	228
Hu-BGc-Aut2	1 September 2003	30 November 2003	90	9.4	32	151	0.0	31.2	72	43
Hu-BGc-Win2	1 December 2003	29 February 2004	90	0.8	39	108	0.0	13.2	3	−69
Hu-BGc-Spr2	1 March 2004	31 May 2004	91	10.0	36	199	0.0	3.1	−2	51
Hu-BGc-Sum3	1 June 2004	31 August 2004	91	19.5	23	232	0.0	nd	121	176
Hu-BGc-Aut3	1 September 2004	30 November 2004	90	12.5	34	181	0.0	17.4	134	84
Hu-BGc-Win3	1 December 2004	31 December 2004	30	1.9	43	34	0.0	nd	−30	−54
Hu-BGg-Sum1	1 August 2002	31 August 2002	30	20.9	31	59	1.0	nd	894	193
Hu-BGg-Aut1	1 September 2002	30 November 2002	90	12.1	30	123	0.2	nd	143	79
Hu-BGg-Win1	1 December 2002	28 February 2003	89	1.3	42	105	0.3	nd	2	−62
Hu-BGg-Spr1	1 March 2003	31 May 2003	91	10.8	26	64	0.8	21.2	115	62
Hu-BGg-Sum2	1 June 2003	31 August 2003	91	23.5	11	77	0.3	nd	96	228
Hu-BGg-Aut2	1 September 2003	30 November 2003	90	9.4	32	151	0.5	30.3	72	43
Hu-BGg-Win2	1 December 2003	29 February 2004	90	0.8	39	108	0.2	16.5	−2	−69
Hu-BGg-Spr2	1 March 2004	31 May 2004	91	10.0	36	199	0.6	2.1	18	51
Hu-BGg-Sum3	1 June 2004	31 August 2004	91	19.5	23	232	0.6	nd	121	176
Hu-BGg-Aut3	1 September 2004	30 November 2004	90	12.5	34	181	0.5	17.8	152	84
Hu-BGg-Win3	1 December 2004	31 December 2004	30	1.9	43	34	0.0	nd	20	−54
UK-BS-Jul02	1 July 2002	31 July 2002	31	15.0	59	86	3.8	nd	180	117
UK-BS-Aug02	1 September 2002	30 September 2002	30	12.8	61	43	10.4	2.5	181	88
UK-BS-Oct02	1 October 2002	31 October 2002	31	8.9	65	200	6.6	nd	63	37
UK-BS-Nov02	1 November 2002	30 November 2002	30	6.3	80	91	1.1	2.2	219	3
UK-BS-Dec02	1 December 2002	31 December 2002	31	5.9	82	72	1.1	2.8	57	−3
UK-BS-Jan03	1 January 2003	31 January 2003	31	4.3	83	94	0.0	2.0	−444	−24
UK-BS-Feb03	1 February 2003	28 February 2003	28	2.0	78	29	0.0	2.4	−13	−53
UK-BS-Apr03	1 April 2003	30 April 2003	30	8.3	57	44	0.0	2.2	131	29
UK-BS-May03	1 May 2003	31 May 2003	31	10.5	76	108	1.1	nd	56	58
Ei-CA-Aut1	16 September 2004	11 November 2004	56	12.1	49	107	2.0	52	293	78
UK-CPe-Spr1	5 April 2002	31 May 2002	56	9.2	78	67	0.0	8.1	27	41
UK-CPe-Sum1	1 June 2002	31 August 2002	91	14.8	74	337	0.0	9.6	58	115
UK-CPe-Aut1	1 September 2002	30 November 2002	90	9.4	79	332	0.0	11.1	30	44
UK-CPe-Win1	1 December 2002	28 February 2003	89	3.2	100	191	0.0	21.2	6	−37
UK-CPe-Spr2	1 March 2003	31 May 2003	91	7.9	86	180	0.0	8.7	5	24
UK-CPe-Sum2	1 June 2003	31 August 2003	91	15.1	54	121	0.0	11.6	38	118
UK-CPe-Aut2	1 September 2003	30 November 2003	90	9.1	52	210	0.0	12.9	14	40
UK-CPe-Win2	December 2003	29 February 2004	90	3.9	90	275	0.0	8.6	12	−29
UK-CPe-Spr3	1 March 2004	31 May 2004	91	8.3	84	181	0.0	10.4	38	29
UK-CPe-Sum3	1 June 2004	26 August 04	86	15.1	73	388	0.0	nd	90	118
Fr-LAe-Spr1	10 April 2002	5 June 2002	56	11.4	51	176	0.4	27.5	−1	70

Fr-LAe-Sum1	6 June 2002	10 September 02	96	15.4	57	345	1.2	48.8	17	122
Fr-LAe-Aut1	11 September 2002	23 October 2002	42	10.8	49	77	1.1	63.7	81	62
Fr-LAe-Spr2	13 March 2003	27 May 2003	75	8.7	49	77	0.3	32.3	12	35
Fr-LAe-Sum2	28 May 2003	2 September 2003	97	18.0	36	314	1.3	72.5	37	156
Fr-LAe-Aut2	3 September 2003	2 October 2003	29	13.2	41	84	1.0	74.5	21	93
Fr-LAe-Spr3	18 March 2004	26 May 2004	69	5.7	55	0	0.4	63.7	0	−4
Fr-LAe-Sum3	27 May 2004	6 September 04	102	15.3	43	353	1.4	77.8	7	121
Fr-LAe-Aut3	7 September 2004	19 October 2004	42	13.3	48	135	1.1	83.1	1	95
Fr-LAi-Spr1	10 April 2002	19 June 2002	70	15.1	50	229	2.6	22.6	26	118
Fr-LAi-Aut1	1 September 2002	23 October 2002	52	12.1	48	139	2.0	15.5	189	78
Fr-LAi-Spr2	13 March 2003	27 May 2003	75	9.2	47	77	0.6	28.7	28	41
Fr-LAi-Spr3	18 March 2004	23 May 2004	66	5.5	53	0	0.6	44.2	2	−7
Dk-LV1-Grw1	12 April 2002	7 June 2002	56	12.3	53	78	0.0	2.1	43	81
Dk-LV1-Grw2	8 June 2002	20 September 2002	104	18.6	56	238	0.0	2.2	43	163
Dk-LV1-Aut1	21 September 2002	27 November 2002	67	8.5	54	199	0.0	1.5	9	31
Dk-LV1-Win1	28 November 2002	1 March 2003	93	0.7	50	76	0.0	3.6	14	−71
Dk-LV1-Grw3	8 April 2003	11 June 2003	64	10.2	62	114	0.0	11.0	114	54
Dk-LV1-Grw4	1 August 2003	1 September 2003	31	16.5	43	47	0.0	nd	61	137
Dk-LV1-Aut2	7 November 2003	6 December 2003	29	6.4	83	31	0.0	10.1	18	5
Dk-LV1-Grw5	12 March 2004	15 June 2004	95	9.0	67	94	0.0	31.9	24	39
Dk-LV2-Spr1	12 April 2002	20 June 2002	69	13.1	53	101	0.0	11.3	410	92
Dk-LV2-Sum1	21 June 2002	21 August 2002	61	18.6	61	200	0.0	4.5	55	163
Dk-LV2-Aut1	22 August 2002	4 November 2002	74	13.9	60	150	0.0	2.4	12	102
Dk-LV2-Win1	5 November 2002	19 December 2002	44	3.8	60	66	0.0	2.7	6	−30
Dk-LV2-Sum2	22 May 2003	25 August 2003	95	15.9	54	135	0.0	10.1	117	128
Dk-LV2-Aut2	26 August 2003	6 October 2003	41	13.3	58	88	0.0	3.6	10	94
Dk-LV2-Win2	6 October 2003	6 December 2003	61	6.6	77	67	0.0	6.6	16	6
Dk-LV2-Spr3	11 March 2004	15 June 2004	96	8.9	67	94	0.0	35.3	31	37
It-MA-Aut1	2 September 2003	3 October 2003	31	8.6	59	40	0.0	nd	2	33
It-MA-Sum2	4 June 2004	1 September 2004	89	10.9	75	169	0.0	nd	3	64
It-MA-Aut2	2 September 2004	2 October 2004	30	9.5	45	40	0.0	nd	4	45
CH-OEe-Grw1	12 June 2002	14 August 2002	63	19.3	55	253	0.0	0.7	0	173
CH-OEe-Grw2	15 August 2002	26 September 2002	42	17.4	61	159	0.0	0.2	47	148
CH-OEe-Aut1	27 September 2002	30 November 2002	64	9.3	80	449	0.0	0.1	−89	42
CH-OEe-Win1	1 December 2002	28 February 2003	89	2.2	82	283	0.0	nd	−1	−50
CH-OEe-Grw3	1 March 2003	2 June 2003	93	10.5	55	177	0.0	nd	33	58
CH-OEe-Grw4	3 June 2003	3 August 2003	61	21.9	33	127	0.0	nd	219	207
CH-OEe-Grw5	4 August 2003	12 October 2003	69	17.1	32	244	0.0	nd	−164	144
CH-OEe-Aut2	13 October 2003	30 November 2003	48	5.7	59	103	0.0	nd	−323	−5
CH-OEe-Win2	1 December 2003	29 February 2004	90	1.7	72	362	0.0	nd	−130	−57
CH-OEe-Grw6	1 March 2004	6 June 2004	97	9.0	58	241	0.0	nd	−37	38
CH-OEe-Grw7	7 June 2004	27 August 2004	81	19.2	54	269	0.0	nd	231	171
CH-OEe-Grw8	28 August 2004	3 November 2004	67	15.0	68	253	0.0	nd	−16	117
CH-OEi-Win1	4 March 2004	11 March 2004	7	2.6	67	8	0.0	nd	904	−46

[a] Measured at −5 cm; Spr: spring; Sum: summer; Aut: autumn; Win: winter; Grw: growth phase.
[b] From Eq. (1).

Appendix B. Breakdown of annual cumulative N_2O fluxes: fertilization events

Site-event	Date		Duration (days)	Soil T[a] (°C)	WFPS[a] (%)	Rain (mm)	GD (LSU ha^{-1})	Soil min. N (mg N kg^{-1})	N_2O flux (g N ha^{-1})	N fertile (kg N ha^{-1})	EF (meas) (%)	EF (fit) (%)
	Start	End										
UK-BS-NPK1	1 June 2002	30 June 2002	30	14.5	61	103	0.3	nd	2849	120	2.4	0.6
UK-BS-NPK2	1 August 2002	31 August 2002	31	15.3	72	156	5.6	4.7	1488	50	2.8	3.4
UK-BS-AN/NPK	1 March 2003	31 March 2003	31	5.3	76	32	0.0	nd	585	136	0.5	0.2
UK-BS-NPK4	1 June 2003	30 June 2003	30	14.1	55	36	1.5	3.3	1	48	0.0	0.1
Ei-CA-CAN1	2 April 2004	24 May 2004	52	9.8	60	102	0.0	32	977	128	0.8	0.1
UK-CPi-AN1	30 April 2002	3 May 2002	3	8.5	79	10	0.0	12.5	191	100	0.2	0.5
UK-CPi-AN2	20 June 2002	23 July 2002	33	14.8	66	35	0.0	22.3	178	100	0.1	0.8
UK-CPi-AN3	28 August 2002	26 September 2002	29	13.1	68	72	0.0	18.6	2942	100	3.2	1.0
Fr-LAi-AN2	28 May 2003	3 July 2003	36	18.7	42	131	2.7	56.0	147	84	0.1	0.4
Fr-LAi-AN3	4 July 2003	17 August 2003	44	19.4	36	88	2.6	124.5	463	50	0.9	0.2
Fr-LAi-AN4	18 August 2003	6 October 2003	49	15.0	41	169	2.0	87.9	124	40	0.3	0.2
Fr-LAi-AN5	24 May 2004	7 July 2004	44	14.0	39	55	3.5	54.4	16	69	0.0	0.1
Fr-LAi-AN6	8 July 2004	16 August 2004	39	16.8	32	147	2.5	37.9	72	67	0.1	0.3
Fr-LAi-AN7	17 August 2004	17 October 2004	61	14.3	46	279	2.3	52.9	148	40	0.4	0.2
Nl-LE-Spr1	16 May 2002	17 June 2002	32	16.2	69	52	0.0	nd	720	41	1.6	1.3
Nl-LE-Sum1A	19 June 2002	15 July 2002	26	16.2	70	81	0.0	nd	1900	26	7.6	2.1
Nl-LE-Sum1B	23 July 2002	13 August 2002	21	18.8	81	102	3.1	nd	2068	54	4.0	5.8
Nl-LE-Sum1C	14 August 2002	3 September 2002	20	18.1	84	54	0.0	nd	959	44	2.2	2.4
Nl-LE-Aut1	4 September 2002	6 October 2002	32	14.7	85	77	0.0	nd	353	26	1.0	1.1
Nl-LE-Spr2A	19 March 2003	19 May 2003	61	8.4	89	106	0.0	nd	346	112	0.3	0.1
Nl-LE-Spr2B	20 May 2003	12 June 2003	23	16.8	89	37	2.8	nd	1792	70	2.7	0.6
Nl-LE-Sum2A	13 June 2003	9 July 2003	26	17.6	77	34	0.0	nd	867	72	1.2	1.5
Nl-LE-Sum2B	10 July 2003	16 August 2003	37	19.4	57	53	0.0	nd	107	24	0.0	0.3
Nl-LE-Spr3A	28 April 2004	14 May 2004	16	11.1	81	58	0.0	nd	1152	159	0.7	1.0
Nl-LE-Spr3B	14 May 2004	21 June 2004	38	16.3	70	62	0.0	nd	1063	29	3.4	1.4
Dk-LV1-NPKS1	1 March 2003	7 April 2003	37	2.2	53	12	0.0	29.2	109	100	0.1	0.0
Dk-LV1-NPKS2	15 June 2003	31 July 2003	46	16.1	57	95	0.0	5.2	99	105	0.0	0.2
Dk-LV1-Fym1	1 September 2003	22 October 2003	51	11.5	61	87	0.0	5.3	97	73	0.0	0.3
Dk-LV1-AS1	1 February 2004	11 March 2004	39	1.0	73	22	0.0	31.1	0	75	0.0	0.1
Dk-LV2-AS1	5 April 2003	21 May 2003	46	8.3	59	95	0.0	17.5	125	29	0.1	0.1
CH-OEi-AN1	1 July 2002	9 July 2002	7	20.0	43	23	0.0	nd	42	35	0.1	0.4
CH-OEi-Slu1	19 August 2002	24 September 2002	36	17.6	59	139	0.0	0.1	1564	105	1.8	0.9
CH-OEi-AN2	30 September 2002	31 October 2002	30	10.8	77	204	0.0	1.3	1102	30	4.4	2.5
CH-OEi-Slu2	18 March 2003	22 March 2003	4	5.7	48	0	0.0	nd	7	113	0.0	0.0
CH-OEi-AN3	2 June 2003	16 July 2003	43	24.8	35	46	0.0	nd	1295	15	7.1	0.5
CH-OEi-Slu3	18 August 2003	10 September 2003	23	19.3	27	77	0.0	nd	112	82	0.4	0.4
CH-OEi-Slu4	17 March 2004	30 March 2004	13	6.3	66	30	0.0	nd	46	65	0.1	0.3
CH-OEi-AN4	17 May 2004	27 May 2004	10	16.3	48	13	0.0	nd	292	30	1.1	0.1
CH-OEi-Slu5	1 July 2004	12 July 2004	10	18.7	51	57	0.0	nd	284	60	0.4	0.7
CH-OEi-AN5	31 August 2004	21 September 2004	20	18.4	57	39	0.0	nd	351	30	1.3	0.3

AN: ammonium nitrate; AS: ammonium sulfate; CAN: calcium ammonium nitrate; NPK(S): synthetic fertilizer containing N, P, K (and S); GD: grazing density; Slu: (cattle) slurry; Fym: farmyard manure; Spr: spring; Sum: summer; Aut: autumn. From Eq. (4).

[a] Measured at −5 cm.

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