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Atmospheric Measurement Techniques

Nitrous oxide emissions from managed grassland: a comparison of eddy covariance and static chamber measurements

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Abstract. Managed grasslands are known to be an important source of N_2O with estimated global losses of 2.5 Tg N_2O-N yr^{-1}. Chambers are to date the most widely used method to measure N_2O fluxes, but also micrometeorological methods are successfully applied. In this paper we present a comparison of N_2O fluxes measured by non-steady state chambers and eddy covariance (EC) (using an ultra-sonic anemometer coupled with a tunable diode laser) from an intensively grazed and fertilised grassland site in South East Scotland. The measurements were taken after fertilisation events in 2003, 2007 and 2008. In four out of six comparison periods, a short-lived increase of N_2O emissions was observed after mineral N application, returning to background level within 2–6 days. Highest fluxes were measured by both methods in July 2007 with maximum values of 1438 ng N_2O-N m^{-2} s^{-1} (EC) and 651 ng N_2O-N m^{-2} s^{-1} (chamber method). Negative fluxes above the detection limit were observed in all comparison periods by EC, while with chambers, the recorded negative fluxes were always below detection limit. Median and average fluxes over each period were always positive. Over all 6 comparison periods, 69 % of N_2O fluxes measured by EC at the time of chamber closure were within the range of the chamber measurements. N_2O fluxes measured by EC during the time of chamber closure were not consistently smaller, neither larger, compared to those measured by chambers: this reflects the fact that the different techniques integrate fluxes over different spatial and temporal scales. Large fluxes measured by chambers may be representing local hotspots providing a small contribution to the flux measured by the EC method which integrates over a larger area. The spatial variability from chamber measurements was high, as shown by a coefficient of variation of up to 139 %. No diurnal pattern of N_2O fluxes was observed, possibly due to the small diurnal variations of soil temperature. The calculation of cumulative fluxes using different integration methods showed EC data provide generally lower estimates of N_2O emissions than chambers.

1 Introduction

At the global scale, soils are the most important source of the greenhouse gas nitrous oxide (N_2O), with an estimated emission of 9.5 Tg N_2O-N yr^{-1} (65 % of total global emissions), 1 Tg of which originates from temperate grasslands (IPCC, 2001). The two mechanisms principally responsible for N_2O emissions from soils are the microbial processes nitrification and denitrification which are mainly controlled by oxygen supply (and hence soil moisture), temperature, the availability of nitrogen and mineralizable carbon, as well as soil pH and soil microbial community (e.g. Granli and Bockman, 1994; Smith et al., 1998; Dobbie et al., 1999). Emissions are highly variable in space and time due to small scale changes of substrates and oxygen supply in the soil as well as changing environmental and management conditions over time. In temperate climates N_2O emissions have been shown to be largely event driven with rainfall, water filled pore space (WFPS) and nitrogen fertilisation being critical factors (e.g. Flechard et al., 2005, 2007; Jones et al., 2007). Annual emissions of N_2O from agricultural land, especially grazed grassland, are therefore difficult to quantify and the uncertainty surrounding national inventories and global estimates of agricultural N_2O emissions is still high (Grant and Pattey, 2003; Dejardins, 2004; Flechard et al., 2007).

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All data sets used to define IPCC N_2O emission factors, which are used for official estimates of annual N_2O fluxes from agricultural ecosystems, originate from manually operated static chamber measurements (Bouwmann, 1996; IPCC, 1997). Manually operated static chambers are fairly inexpensive, do not require power (unless a fan is used) and are simple to operate. They provide valuable information comparing different treatments or assessing the spatial variability (e.g. Clayton et al., 1994; Velthof et al., 1996; Jones et al., 2007). However, their coverage is limited over space and time. The cover area per measurement is usually less than 1 m^2 and measurements are rarely taken more than once per day. Thus, this method is not well suited to describe daily variations or short-lived emission pulses induced by events such as rainfall, fertilization, re-wetting of dry soil and freeze-thaw. It is therefore not surprising the uncertainty of annual flux estimates from manually operated chambers is as high as 50 % due to spatial and temporal variability (Flechard et al., 2007). Further downsides of chambers are that they are intrusive, as they have to be inserted into the soil and this may temporarily change C and N cycling by disturbing the soil and cutting roots; their presence in the field may affect the grazing behaviour of animals, and they modify the environmental conditions (wind, temperature) during the measurement (e.g. Ambus and Christensen, 1994; Davidson et al., 2002). Furthermore, it has been shown that static chambers potentially underestimate fluxes if no fan is used to mix the chamber headspace (Pumpanen et al., 2004; Christiansen et al., 2011).

An alternative, less disruptive approach in measuring fluxes at high time resolution at field scale level is offered by micrometeorological techniques. These methods require a uniform surface to be investigated, wind, temperature and gas concentrations at one or more points above the soil-vegetation surface, using high sensitivity gas analysers. The area over which a flux can be integrated ranges from 0.01–1 km^2, depending on the height of the sampling tower. However, this requires a uniform surface, which in many agricultural ecosystems may be a limitation. Further downsides of micrometeorological techniques applied to N_2O are that they are more expensive and require higher expertise than static chambers. The most widely used micrometeorological technique for N_2O flux measurements is the eddy covariance (EC) method, but also the Relaxed Eddy Accumulation (REA) and the flux gradient method have been applied to N_2O emission measurements (see e.g. Skiba et al., 1996; Pattey et al., 2006; Desjardin et al., 2010). N_2O has been measured successfully in agricultural ecosystems by EC since the development of suitable high frequency fast response N_2O analysers, such as lead salt tunable diode lasers (e.g. Smith et al., 1994; Wienhold et al., 1995; Fowler et al., 1995; Laville et al., 1999; Di Marco et al., 2004) and more recently, quantum cascade lasers (e.g. Neftel et al., 2007; Kroon et al., 2010).

The objectives of this paper are to assess the suitability of manual chambers and eddy covariance as methods for measuring N_2O emissions at the field scale, both in terms of instantaneous fluxes in response to trigger events, and in terms of time-integrated (cumulative) fluxes over several weeks with a view to deriving emission factors, contributing to the improvement of national inventories.

We present a comparison of N_2O flux data sets measured by manually operated non-steady state chambers and eddy covariance technique from an intensively grazed and fertilised grassland site in the South East of Scotland. The measurements were taken after six mineral N fertilisation events in 2003, 2007 and 2008 with comparison periods lasting between 3 and 29 days.

2 Materials and methods

2.1 Site description

The Easter Bush measurement site is located in a rural area 10 km south of Edinburgh, Scotland UK (3°12′ W, 55°52′ N, 190 m a.s.l.). The site consists of two intensively-managed grassland fields of approximately 5 ha each, here referred to as "South" and "North" fields (see Fig. 1, for a more detailed description of the site refer to Milford et al., 2001). The equipment for eddy covariance measurements was situated on the boundary between the two fields. This enabled eddy covariance flux measurements from the South field in south westerly wind and from the North field in north easterly wind, along the prevailing wind direction. Over the years 2003–2008, the fields received mineral fertiliser of an average 183 kg N ha^{-1} yr^{-1} split into three to four fertiliser applications per year. Simultaneous measurements between EC and chamber methods of N_2O fluxes were made at fertilisation events on six occasions (see Table 1). In 2003, fourteen chambers were placed in the South field while in 2007 and 2008 four chambers were placed in the South field and four chambers in the North field. Both fields were continuously grazed at an average grazing intensity of 0.70 livestock units ha^{-1}, where one live stock unit (LSU) corresponds to a dairy cow with a live weight of 600 kg (Farm management Handbook SAC, 1995). In our study, grazing animals consisted of sheep (60 kg live weight, LSU 0.1), lambs (5–45 kg live weight, LSU 0.04) and occasionally heifers in calve (450 kg live weight, LSU 0.75). The soil was an imperfectly drained Macmerry soil series, Rowanhill soil association (eutric cambisol) with a pH (in H_2O) of 5.1 and a clay fraction of 20–26 %. The main grass species was Italian ryegrass (*Lolium perenne*). The average annual rainfall (2003–2008) was 994 mm and the annual mean temperature was 9.04 °C with a maximum monthly mean of 16.8 °C occurring in July 2003 and a minimum of 3.5 °C in February 2005.

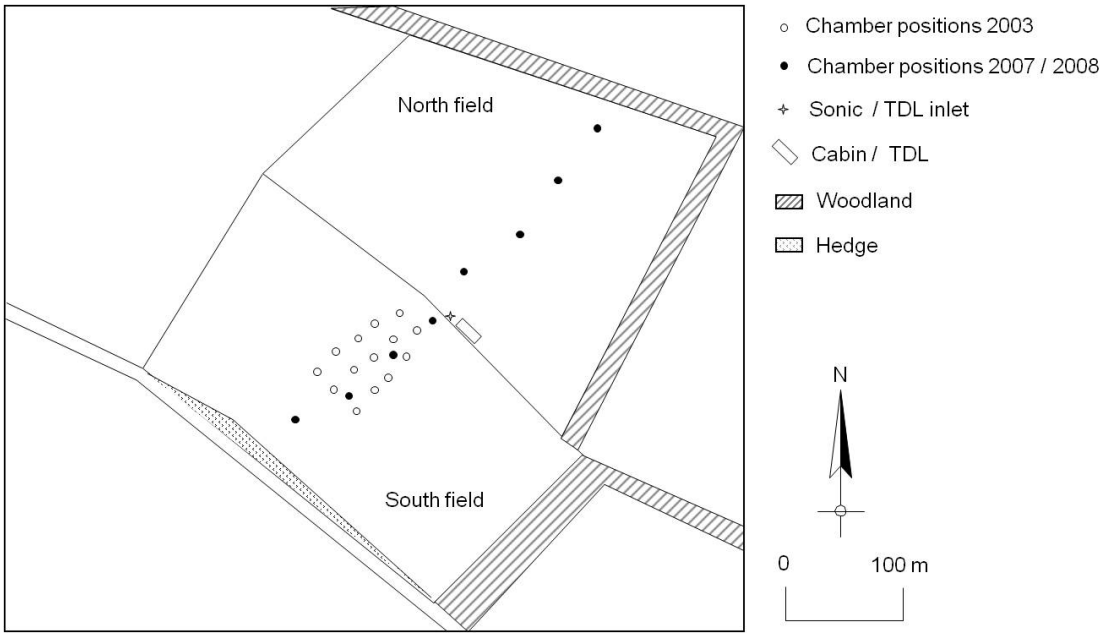

Fig. 1. Site diagram of the study field Easter Bush, showing locations of static chambers in the South and North field in 2003 and 2007/2008, micrometeorological mast (eddy covariance inlet and sonic position) and cabin (containing TDL) on the boundary of the two fields and prevailing wind directions.

Table 1. Overview of comparison periods of eddy covariance and chamber N_2O flux measurements, fertiliser application dates, amount of N applied, average air and soil temperature (T_{air}, T_{soil}), average soil water content (SWC), average water filled pore space (WFPS) and total rainfall.

Comparison period	Duration [days]	Fertilisation date	N fertiliser input [kg N ha^{-1}]	T_{air} [°C]	$T_{soil(7.5cm)}$ [°C]	SWC $_{(7.5cm)}$ [%]	WFPS $_{(7.5cm)}$ [%]	rain [mm]
11.6.–13.6. 2003	3	10.6. 2003	48	14.9	13.8	35	66	2
15.3.–3.4. 2007	20	14.3. 2007	69	5.9	5.6	47	85	53
10.5.–7.6. 2007	29	16.5. 2007	51.75	10.3	10.9	41	75	120
10.7.–27.7. 2007	18	11.7. 2007	51.75	13.5	14.0	45	84	65
14.5.–26.5. 2008	13	13.5. 2008	51.75	10.5	11.8	36	68	18
20.6.–7.7. 2008	17	18.6. 2008	51.75	12.4	12.4	39	72	85

2.2 Chamber measurements of N_2O fluxes

Static chambers, each covering an area of 0.1256 m^2, were used for the enclosure technique. Each chamber consisted of a 0.2 m long PVC ring (diameter 0.4 m) with a 0.045 m wide PVC flange fitted to the outward facing end (Clayton et al., 1994). The ring was inserted into the soil to approx. 3 cm depth giving a headspace volume of 21.4 l. Chambers were closed for 60 min with an aluminium lid fitted with draft excluder. Samples of 200 ml were collected by syringe into Tedlar bags at the beginning and at the end of the closure time through a three-way tap which was fitted into the lid. The syringe was flushed three times before sampling in order to mix the chamber air. In the laboratory, samples were transferred to glass vials and analyzed for N_2O using a Hewlett Packard 5890 series II gas chromatograph (Agilent Technologies, Stockport, UK), fitted with an electron capture detector (detection limit for N_2O 33 ppbV). Chamber closure and gas sampling were carried out between 10:00 h and 12:00 h. Fluxes were calculated as

$$F = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \quad (1)$$

where V and A are the volume and surface area of the chamber, ΔC is the difference in the N_2O concentration between the start and the end gas sample, and Δt is the closing time, so $\Delta C/\Delta t$ is the slope of the gas concentration change with time. Repeated linearity tests, taking samples every 15 min

over 2 h, were carried out prior to, as well as in between measurement campaigns, showing a linearity of up to 120 min with an average $r^2 = 0.96$. The estimated detection limit for N_2O fluxes measured by the chambers in this campaign was 12 ng N_2O-N m^{-2} s^{-1}. The chambers were removed every two weeks to reduce the chamber effect on the vegetation and soil and allow free grazing. Chambers were re-positioned at least 24 h before measurement, to avoid the influence of the soil disturbance on N_2O production. The grass inside the chambers was always accessible to the animals for grazing, apart from the 1 h period during which chambers were closed for the N_2O measurements. Grazing maintained a canopy height that was always lower than the chamber height (20 cm) and therefore chambers were operational throughout the inter-comparison periods.

2.3 Eddy-covariance measurements of N_2O fluxes

The eddy covariance flux was calculated as the covariance between the N_2O concentration (χ) and the vertical component of the wind speed (w) as:

$$F_\chi = \overline{\chi' w'}. \quad (2)$$

χ' and w' represent the fluctuations around the mean components of concentration and vertical wind speed respectively (see e.g. Kaimal and Finnigan, 1994; Stull, 1988). In order to capture the small scale eddy contribution to the flux, fast response sensors are required to measure the fluctuations in concentrations and wind speed (depending on the height above the surface: typically for grasslands at 5 to 20 Hz). This is achieved using ultra-sonic anemometers for components of turbulence (see e.g. Kaimal and Gaynor, 1991), and by chemical analysers that are able to sense an increasing variety of scalar concentrations at fast rates, such as Tunable Diode Laser absorption spectrometers (TDL) in the case of N_2O (see e.g. Zahniser et al., 1995; Fowler et al., 1995). A fast response ultrasonic anemometer (model USA-1, METEK GmbH, Elmshorn, Germany) was used to measure the three components of the wind at a frequency of 10 Hz. It was mounted on a 2.35 m mast located at the edge between the two fields, with a fetch of approximately 250 m in the prevailing wind direction. The N_2O concentration was measured by a TDL (Aerodyne Research Inc., Billerica, MA, USA) located in a monitoring cabin on the field. An inlet line of Dekabon tubing, 1/4″ OD was placed underneath the transducers of the sonic anemometer, drawing air to the TDL sampling cell at a rate of 15 l min^{-1}. The TDL was operated at a frequency of 5 to 7 Hz and was tuned to use an N_2O adsorption feature at a wave number of 2009.4 cm^{-1}. Daily manual calibrations were applied using an ambient-level standard gas mixture of 320 ppbV, cross-calibrated with a NOAA standard mixture. The detection limit of the TDL was estimated to be 1 ppbV at 1 s averaging time.

A custom made LabView (National Instruments Inc.) program acquired the raw data from the sonic anemometer and the TDL, and calculated online fluxes for each half hour period. A double coordinate rotation was applied to the raw data, offline concentrations were calibrated against the standard gas concentration and were reanalysed to correct for density fluctuations caused by water vapour fluxes according to the method by Webb-Pearman-Leuning (see Webb et al., 1980). The temperature fluctuation component of this WPL correction was ignored as the inlet line was long enough to establish temperature equilibrium. The time-lag between the measurement of the vertical wind component and N_2O concentration was determined from the absolute maximum in their cross-correlation within a pre-defined window (0.7 to 1.7 s on average). According to recent findings (e.g. Taipale et al., 2010), this practice can overestimate the flux (both negative and positive fluxes) if a noisy sensor is used: since that was our case (especially for the 2008 data) we also calculated the fluxes with a fixed time lag (using clear emission fluxes time lags derived from the maximum cross correlation function) and compared the two outcomes.

For a 30 min averaging period the detection limit of the N_2O flux measurement was estimated at 11 ng N_2O-N m^{-2} s^{-1} by flushing zero-N_2O air through the system and measuring the flux. In some instances, the lead salt laser instability affected the concentration measurements, creating variations that do not reflect the real atmospheric turbulence (see also Di Marco, 2005). In order to avoid instrumental artefacts, we calculated the flux detection limit according to the method by Wienhold (Wienhold et al., 1994) for each half hourly flux. The average detection limit ranged between 12.3 ng N_2O-N m^{-2} s^{-1} and 33.6 ng N_2O-N m^{-2} s^{-1} across the measurements campaigns. The events where the flux value was below detection limit were discarded. In order to investigate high frequency losses due to signal attenuation, we applied the Horst formula (see Horst, 1997) which resulted in an average flux loss of 10 %; this result was confirmed by applying a spectral correction on the ogives (as in Ammann et al., 2006) on selected flux events. The ogive analysis applied to all fluxes, by comparison with the sensible heat fluxes curves was used in addition as a rejection criterion, to visually exclude flux values that presented irregularities.

We applied further filters to the data. (i) A spike removal routine was embedded in the re-analysis custom made program (ii) a stationarity filter (see Affre et al., 2000) was applied to the N_2O flux values (iii) the variances of the half-hourly concentrations of N_2O were used to flag periods that presented anomalous variation of concentration. Due to instruments downtime, data coverage for the EC fluxes were: 80 % in June 2003, 82 % in March 2007, 90 % in May 2007, 76 % in June 2007, 30 % in May 2008 and 37 % in July 2008. The remarkable difference between data coverage percentages between 2007 and 2008 is explained by the different lead salt laser source: at the end of 2007 it had to be changed, and the replacement laser diode proved a lot more unstable. Rejection of N_2O fluxes due to quality control

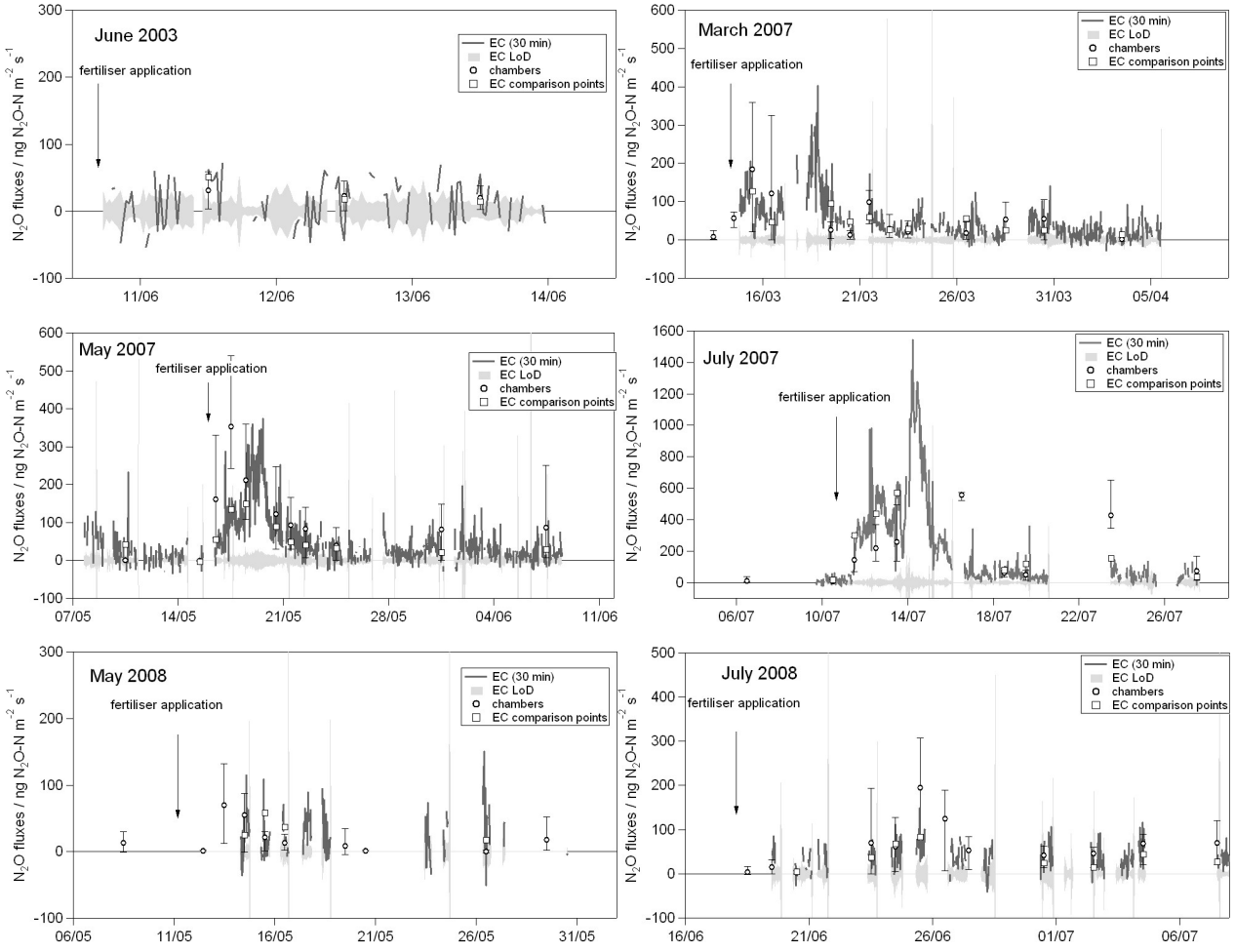

Fig. 2. N_2O fluxes obtained with eddy covariance and static chambers for 6 comparison periods; eddy covariance data are 30 min values (grey line) or values averaged over the one hour period when chambers were closed (between 10:00–12:00, squares). Chamber measurement points represent the average of 14 (2003) or 4 (2007/2008) chambers measured over 1 h (white circles), with error bars representing the range of chamber measurements. Fertiliser applications are indicated with an arrow.

(including bad wind sector, and electronic noise beside the filtering criteria listed above) resulted in a final data capture for the EC fluxes of 69 % in June 2003, 63 % in March 2007, 65 % in May 2007, 63 % in June 2007, 24 % in May 2008 and 23 % in July 2008.

2.4 Additional measurements

Soil temperature and volumetric soil moisture were continuously recorded at four depths (3.5/7.5/15/30 cm) on each field by temperature probes (temperature probe 107, Campbell Scientific, Loughborough, UK) and TDR probes (TDR 100, Campbell Scientific, Loughborough, UK), respectively. Rain was measured by a tipping bucket rain gauge in the middle of the measuring site. Extractable soil mineral N (NH_4^+ and NO_3^-) was determined in samples collected at two depths (0–5 cm and 5–15 cm), collected weekly around fertiliser applications, and samples were frozen at −16 °C until analysis. Soil mineral N content was measured from four bulked soil samples using continuous flow colorimetric analysis of 1 M KCl extracts from field-moist soil using a soil:solution ratio of 1:5, following the method of Crooke and Simpson (1971) and Henriksen and Selmer-Olsen (1970).

2.5 Statistical analysis and calculation of cumulative fluxes

Eddy covariance fluxes were measured every half hour, while chamber fluxes were measured once a day over one hour periods, roughly between 10:00 and 12:00, although data were not collected every day; the data series from half hourly EC fluxes including limit of detection and chambers fluxes are shown in Fig. 2. Table 2 provides a summary of statistics for the fluxes measured by both methods. EC fluxes were averaged over the period of chamber closure: for these comparison points (plotted in Fig. 2 as squares), the selected

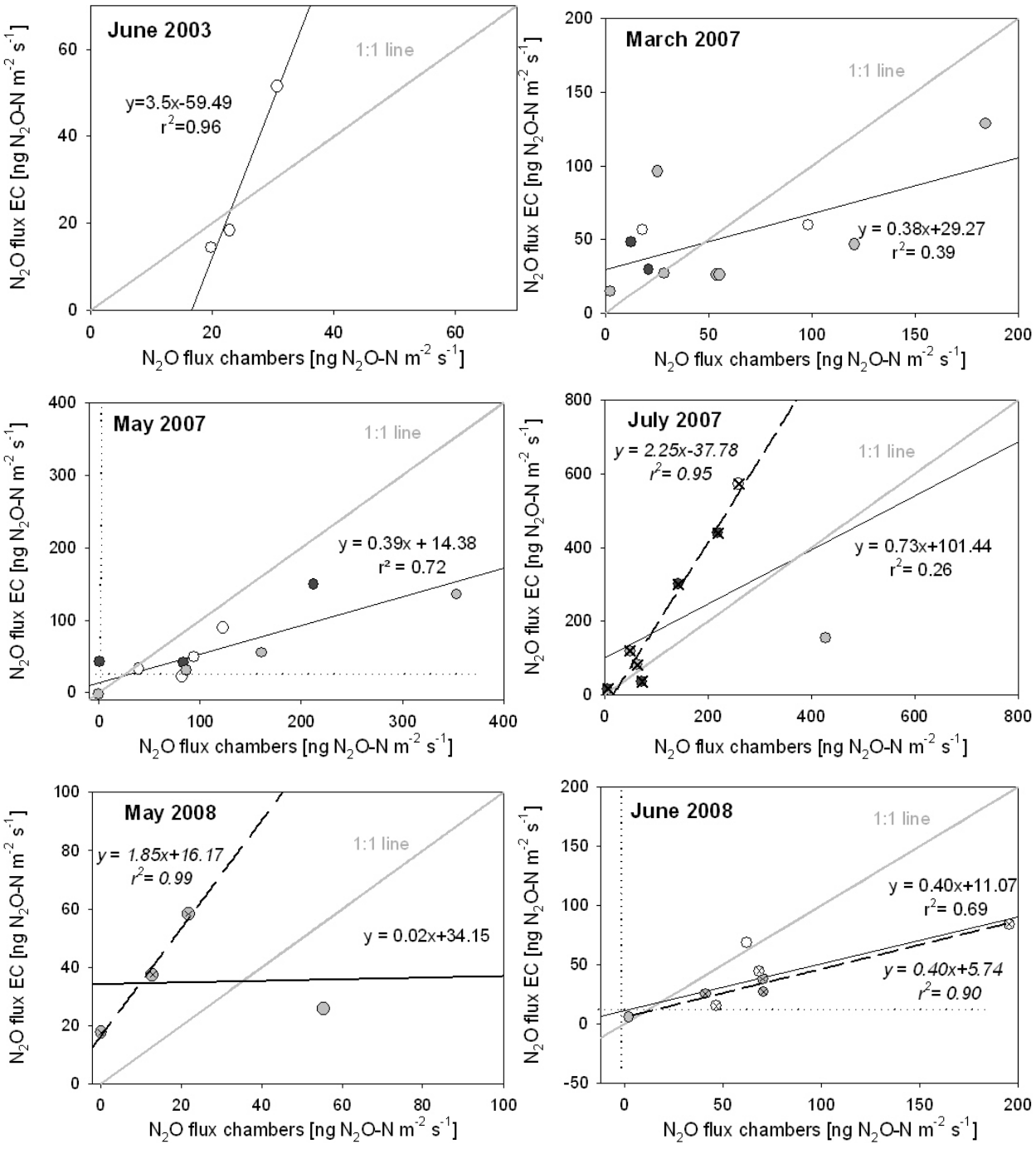

Fig. 3. Comparison of N_2O fluxes measured at the same times (between 10:00 and 12:00) with eddy covariance (EC) and static chambers for each of the 6 comparison periods and data from all comparison periods. Chamber values represent an average of 14 (2003) or 4 (2007/2008) chambers. Circles represent all comparison points, while crosses represent the retained dataset where outliers were removed. Trend lines represent orthogonal regression (continuous line for all comparison points with non italic model equation, dashed line where outliers were removed with italic model equation). Different shades of circles indicate the contribution of the area in which the chambers were situated to the footprint of the EC measurement (open circles = 0–25 %, medium grey = 26–50 %, dark grey = 51–75 %).

chambers were chosen by wind sector selection (amongst 14 chambers in the South field in 2003 and 4 chambers from either South or North field in 2007 and 2008). The probability of all four chambers being within the EC footprint was calculated by footprint analysis, using the approach by Neftel et al. (2008) for data in 2007 and 2008; the results of this analysis are shown in Fig. 3, where a colour scale on the circles indicates the probability of the chambers to be included in the EC footprint.

We then calculated cumulative N_2O fluxes for both methods, using different averaging intervals (hourly, daily, and over the whole period) and assessing their impact on the estimate of the emission factors for inventories. Cumulative N_2O fluxes were calculated over each comparison period using the chambers values as daily averages: all daily fluxes belonging to a comparison period were averaged and multiplied by the number of days (non gap-filled cumulative flux). The missing daily values were then inferred by linear interpolation, and integrated over each period (gap-filled cumulative flux).

The EC cumulative fluxes were calculated using different averaging intervals:

1. EC^a: EC hourly comparison points (measured during chamber closure) were used as daily values, averaged and multiplied by the number of days in each comparison period.

2. EC^b: EC half hourly fluxes were averaged daily, averaged again and multiplied by the number of days in each period.

3. EC^c: half hourly EC fluxes were averaged over each comparison period.

Similarly to the chambers, the cumulative fluxes from the EC data were calculated from non gap-filled (as seen above) and gap-filled data: if half-hour fluxes were missing, the values were inferred by linear interpolation of previous and following data. For the daily fluxes EC^b and EC^a, if no 30 min values were available for 24 h, the missing daily value was calculated by linear interpolation of the previous and following daily value. All cumulative fluxes are listed in Table 3, for gap-filled and non-gap-filled data.

The cumulative fluxes from the chambers were then compared to the three different cumulative fluxes from EC, for each comparison period, using orthogonal regression (see Fig. 3) to avoid biasing the outcome towards one method to the disadvantage of the other.

3 Results

The length of the different comparisons ranged between 3 and 29 days and the rate of N applications varied between 48 and 69 kg N ha^{-1} per period (see Table 1): a variety of environmental conditions was covered, reflected by the wide range of the measured N_2O fluxes. Rainfall varied between 2 and 120 mm per period, corresponding to an average of 0.7 to 4.1 mm of rainfall per day. Soil water content (SWC) was lowest in June 2003 (35 %) and May 2008 (36 %), and highest in March 2007 (47 %), corresponding to water filled pore space values (WFPS) of 65 %, 66 % and 87 %, respectively. Average soil temperatures ranged from 5.6 °C (March 2007) to 14.0 °C (July 2007).

3.1 Magnitude and variability of N_2O fluxes

Throughout the manuscript, positive values represent emission, and negative values deposition fluxes. An increase of N_2O emission after the N application was observed after all fertilization events in 2007 and 2008 by both methods (see Fig. 2). Fluxes declined to background levels (here defined as average daily flux below 50 ng N_2O-N m^{-2} s^{-1}) after 2 to 6 days. No response in N_2O emissions to fertilizer input was observed in June 2003 by either method. Highest fluxes were measured in July 2007, with maximum values of 1438 ng N_2O-N m^{-2} s^{-1} measured by EC on the 14 July, and 651 ng N_2O-N m^{-2} s^{-1} measured by the chambers on the 23 July. During this period the average soil temperature was 14.0 °C, the highest of all comparison periods, and the soil water content (SWC) was 45 %, corresponding to a WFPS of 83 %. In June 2003 and May 2008 fluxes were generally small with maximum values reaching 81.2 ng N_2O-N m^{-2} s^{-1} measured by EC and 91 ng N_2O-N m^{-2} s^{-1} measured by chamber methods in 2003, while corresponding values in May 2008 were 150.9 ng N_2O-N m^{-2} s^{-1} and 87.8 ng N_2O-N m^{-2} s^{-1}. During both these periods soil conditions were dry (35 % and 36 % SWC, respectively) with an average daily rainfall of 0.7 and 1.4 mm respectively, the lowest of all comparison periods.

Negative fluxes were observed in all events by EC while by chamber method negative fluxes were not seen in June 2003 and July 2007. N_2O uptake was observed in 5 % of all 30 min EC data (ranging from 2–25 %). Largest negative values were measured in 2003 with up to −67 ng N_2O-N m^{-2} s^{-1} by EC, whereas with the chamber method largest negative fluxes of only −3.1 ng N_2O-N m^{-2} s^{-1} were measured in March 2007. For EC data, 5 % of all measured fluxes were negative above the calculated detection limit, while for chamber measurements negative fluxes were always below the detection limit (4.4 % of all chamber measurements resulted negative).

The variation between maximum and minimum fluxes measured by EC on days immediately after N application, when fluxes were above background levels, was on average 378 ng N_2O m^{-2} s^{-1}, compared to an average variation of 81 ng N_2O m^{-2} s^{-1}on days where fluxes were at background levels. However, no diurnal patterns with minimum fluxes at night and maximum fluxes at midday could be seen at any day in any comparison period and no correlation could be found between N_2O fluxes and soil temperature or soil

Table 2. Statistics of N_2O fluxes from chambers and eddy covariance (EC) measurements for all 6 comparison periods. Numbers in brackets represent the number of chambers included in the comparison. *EC points* are eddy covariance hourly averages during chamber sampling (between 10:00 and 12:00); *EC all* are half hourly eddy covariance fluxes during the comparison period. The Coefficient of Variation is averaged over all measurements (30 min or daily values).

Comparison period	Method	N	N_2O flux [ng N_2O-N m^{-2} s^{-1}]						
		no. of values	min	25 %	mean	median	75 %	max	CV %
11.6.–13.6. 2003	chambers (15)	45	0.4	6.9	24.5	17.9	35.4	91.0	108.3
	EC points	3	14.4	16.4	28.1	18.4	34.9	51.4	72.4
	EC all	100	−67.4	−17.0	12.2	18.4	40.6	81.2	283.0
15.3.–3.4. 2007	chambers (4)	44	−3.1	7.7	56.4	27.3	70.1	359.1	139.3
	EC points	11	14.6	26.6	50.8	46.7	58.0	128.7	67.7
	EC all	574	−30.5	13.1	47.3	31.7	60.9	403.5	115.4
10.5.–7.6. 2007	chambers (4)	44	−2.6	7.5	112.3	84.5	153.7	540.5	109.4
	EC points	11	−2.4	31.4	58.6	42.1	72.4	149.5	80.7
	EC all	861	−34.1	10.6	44.6	25.9	59.3	314.4	129.8
10.7.–27.7. 2007	chambers (4)	32	3.1	45.1	154.9	97.0	207.9	651.2	102.6
	EC points	8	16.2	70.3	215.1	137.0	335.5	572.6	94.2
	EC all	554	−57.0	27.7	260.2	64.1	290.7	1438.1	74.9
14.5.-26.5. 2008	chambers (4)	16	−1.7	1.5	22.6	12.0	30.3	87.8	125.2
	EC points	4	17.7	23.7	34.8	31.6	42.6	58.3	50.7
	EC all	111	−51.2	3.7	29.3	22.2	55.5	150.9	125.2
20.6.–7.7. 2008	chambers (4)	32	−0.18	14.2	69.7	56.1	90.0	308.5	104.0
	EC points	8	5.8	22.8	38.7	32.6	50.7	84.4	68.8
	EC all	219	−42.6	17.6	42.8	39.1	59.4	371.3	96.9

moisture on any day. The difference between average night (20:00–08:00) and day (08:00–20:00) time emissions was never significant, indicating that other drivers (time after fertilizer application, or rain events) played a more important role than parameters that are subject to a diurnal cycle (temperature, turbulence, heat fluxes).

Over all comparison periods, the largest N_2O fluxes amounted to 1438 ng N_2O-N m^{-2} s^{-1}in July 2007 (see Table 2). Despite the observed negative fluxes, median and average fluxes over each period were always positive. Median N_2O fluxes ranged from 12.0 to 97 ng N_2O-N m^{-2} s^{-1} for chamber methods, from 18.4 to 137 ng N_2O-N m^{-2} s^{-1} for the corresponding EC comparison points, and from 18.4 to 64.1 ng N_2O-N m^{-2} s^{-1} for all EC data. Mean fluxes were on average 2.1 times larger than median fluxes, indicating that fluxes were not normally distributed.

The variability of N_2O fluxes was expressed as coefficient of variation (defined here as the ratio between the standard deviation and the mean, expressed in percentage: CV $\% = (\sigma/\mu) \times 100$) calculated for both measuring techniques. When looking at fluxes during chamber closure, the CV for chamber measurements was always higher than for EC (the highest was measured in March 2007 at 139.3 %). The same can be said for the overall half-hourly N_2O EC fluxes, exception made for the periods of June 2003 and May 2008, where the variation of the overall half-hourly N_2O EC fluxes was higher compared to the chambers, with the highest CV observed in June 2003 at 283 %.

3.2 Comparison of fluxes during chamber closure time

The range of N_2O fluxes measured at the same time by different chambers varied widely. It was largest on the 15 March 2007, at 338 ng N_2O-N m^{-2} s^{-1}, immediately after fertilizer application and smallest on the 10 May 2007, at 2 ng N_2O-N m^{-2} s^{-1}, five days before fertilizer application. EC fluxes during chamber closure were within the range of the chamber measurements in 69 % of the cases over the 6 comparison periods (ranging from 25 % in May 2008 to 100 % in June 2003).

Scatter-plots showing orthogonal regression between chamber and EC measurements made during the same sampling hours are shown in Fig. 3 for all periods. The number of points per period varied from 3 (June 2003) to 11 (May–June 2007, July 2007). In 6 out of 6 comparison periods there was a positive correlation between values from both methods. In June 2003 and May 2008 EC fluxes were higher compared to chamber measurements. For all other comparison periods it was the opposite, with EC values being 38 % ($r^2 = 0.39$), 39 % ($r^2 = 0.72$), 73 % ($r^2 = 0.26$) and 40 % ($r^2 = 0.69$) of the chambers for March, May and June 2007 and July 2008, respectively. The elimination of one outlier in July 2007 changed the story radically, with EC values being 225 % ($r^2 = 0.95$) of chamber measurements. In May 2008 the regression was very close to zero, but the removal of one outlier improved the correlation (r^2 from 0.2 to 0.99) and clearly set the EC values above the chambers.

Table 3. Cumulative N_2O fluxes from chambers and eddy covariance for all 6 periods. Fluxes were calculated using both non gap-filled and gap-filled data. Values in brackets represent standard deviations amongst 14 (2003) or 4 (2007/2008) chambers.

Comparison period	Method	Cumulative N_2O flux [kg N ha^{-1}comparison $period^{-1}$]	
		Non-gap-filled data	gap-filled data
11.6.-13.6. 2003	chambers	0.06 (±0.05)	0.06 (±0.05)
	EC[a]	0.07	0.07
	EC[b]	0.032	0.032
	EC[c]	0.032	0.038
15.3.–3.4. 2007	chambers	0.98 (±0.45)	0.85 (±0.40)
	EC[a]	0.834	0.791
	EC[b]	1.003	1.003
	EC[c]	0.935	0.872
10.5.–7.6. 2007	chambers	2.05 (±1.22)	2.02 (±1.03)
	EC[a]	1.418	1.037
	EC[b]	0.89	0.92
	EC[c]	1.05	0.92
10.7.–27.7. 2007	chambers	2.41 (±0.7)	2.89 (±0.74)
	EC[a]	2.94	2.69
	EC[b]	2.04	2.18
	EC[c]	2.60	2.18
14.5.–26.5. 2008	chambers	0.25 (±0.17)	0.13 (±0.09)
	EC[a]	0.58	0.68
	EC[b]	0.43	0.43
	EC[c]	0.45	0.47
20.6.–7.7. 2008	chambers	1.14 (±0.56)	1.26 (±0.60)
	EC[a]	0.90	0.86
	EC[b]	0.68	0.95
	EC[c]	0.69	0.95

[a] Using only eddy covariance comparison points (over chamber closure times, between 10:00 h and 12:00 h), [b] using daily averages calculated from half hourly fluxes by eddy covariance, [c] using all eddy covariance 30 min data.

The elimination of two outliers in June 2008 increased r^2 from 0.69 to 0.90, but did not change the story, EC fluxes being still 40 % of chambers ones. Overall, EC fluxes were 70 % of the fluxes from chambers.

3.3 Cumulative fluxes

Cumulative fluxes were calculated for each comparison period for both measuring techniques (see Table 3 for a summary). In the literature, cumulative fluxes are often calculated from non-gap-filled data, by averaging all data and multiplying the average by the number of time steps. They can also be calculated by summing up gap-filled data (by linear interpolation) or by a combination of both integration methods (e.g. if fluxes are divided into "triggered emission events" and "background fluxes", see Flechard et al., 2005). To investigate the influence of the integration method on cumulative flux values and therefore on emission factors, we calculated cumulative N_2O fluxes by both frequently used integration methods. For chamber measurements, using non gap-filled data led to larger cumulative fluxes in 4 out of the 6 comparison periods; the differences induced by the integration method ranged from 0 (June 2003) to a factor 2 (May 2008). For EC measurements differences induced by the integration method ranged from 0 % (June 2003, EC[a]) to 50 % (June 2003, EC[c]). Over all comparison periods fluxes from non-gap-filled data represented 83 % of fluxes from gap-filled data for chamber measurements ($r^2 = 0.97$), 111 % for EC[a] ($r^2 = 0.97$), 92 % for EC[b] ($r^2 = 0.97$) and 120 % for EC[c] ($r^2 = 0.96$).

Cumulative fluxes calculated from EC[a] were within one standard deviation of the chamber measurements for all comparison periods with the exception of May 2008. Cumulative EC[a] fluxes represented 72 % of chamber fluxes ($r^2 = 0.81$) when using gap-filled data. Excluding June 2003 and May 2008, all cumulative fluxes from chambers were larger than EC[a] fluxes (up to 1.9 times), when using gap-filled data.

Cumulative fluxes calculated from both gap-filled and non-gap-filled EC[a] were mostly larger than EC[b] except for March 2007 and June 2008 (i.e. remove gap-filled), when using gap-filled data, EC[a] were 144 % of EC[b]($r^2 = 0.97$). Cumulative fluxes calculated from all data (EC[c]) were the lowest compared to any other EC fluxes or chambers, both

in case of gap-filled and non-gap-filled data: they were 79 % of EC^a, 98 % of EC^b, and 59 % of chambers. The different averaging protocols for EC data have been plotted against the cumulative chamber fluxes in Fig. 4. The highest cumulative fluxes were the EC^a: they show the closest agreement with the chambers fluxes as it is more likely to expect (with a slope of 0.71), considering they represent the same hours of sampling. EC^c and EC^b show a very similar behavior, with lower slopes (0.6). Overall, the EC fluxes provide cumulative estimates that are lower than the chambers at the high end of the emission range, but higher at the lower end.

4 Discussion

There are uncertainties in both chamber and EC approaches. As mentioned above, micro-climate and the concentration gradient between the soil and the atmosphere may be altered within a chamber and their small footprint makes them very sensitive to local soil conditions. It has also been demonstrated that chambers present a problem of underestimation of the fluxes if operated without a fan (see Pumpanen et al., 2004; Christiansen et al., 2011). An important additional uncertainty for chamber measurements in grazed and fertilized grassland systems is their effect on grazing behaviour in and around the chamber, and the statistical variability in the fertilizer application across the field. Eddy-covariance measurements are as well subject to some artefacts: flux losses can arise e.g. from limited sensor response times, damping of fluctuations in the sampling line and spatial separation of wind and concentration measurement (e.g. Moore, 1986; Aubinet et al., 2000). It has more recently been realized that the determination of the time-lag between the measurements of turbulence and N_2O concentration as the lag with the largest cross-correlation (and therefore flux) can overestimate the flux (both negative and positive fluxes) if a noisy sensor is used (e.g. Taipale et al., 2010). In addition, parallel EC flux measurements with duplicate towers over the same site typically show average differences of 20 % between 30 min values, due to statistical variations in turbulence, even for the sensible heat flux, which is derived by the anemometer itself (no time lag, sensor separation or damping). By contrast, long-term averages of duplicated measurements are very close because the statistical variability averages out (e.g. Dämmgen et al., 2005; Nemitz et al., 2009).

These uncertainties are of course very relevant during the data analysis process, and are in this work addressed as much as possible.

However, it is necessary to highlight the difference in magnitude of uncertainties linked to the two approaches, static chambers and eddy covariance. Chamber measurements will always be subject to a huge temporal and spatial variability, which makes it a difficult task to assess an integrated flux with an uncertainty of 50 % or 75 % (with no information on over- or under-estimation). With EC, taking into account all issues discussed above for the time-integrated flux, the uncertainty would be around 20 % (and also more likely to be an underestimate, due to losses).

4.1 Influence of management, soil water and temperature on N_2O fluxes

The magnitude of N_2O fluxes measured by chamber and EC methods in our study are comparable with those measured at other European managed grassland sites (e.g. Flechard et al., 2007), although they are at the top end of observed fluxes. This is likely to be due to the influence of grazing and the specific soil and climatic conditions at our experimental site. As most Scottish soils, the soil at Easter Bush is high in organic matter (12.1 $kg\,m^{-2}$). The high soil organic matter, together with the input of labile C from added dung and urine by grazing animals, is likely to have increased denitrification rates by providing substrates for denitrifiers and by stimulating microbial activity (Granli and Bockmann, 1994; Lessard et al., 1996). Furthermore, grazing leads to compaction of the soil, which has been shown to enhance N_2O production by decreasing oxygen diffusion (Simek et al., 2006). Although the average total annual rainfall at our site is comparable with that across much of central Europe, the rainfall in Scotland is distributed evenly over the year, providing moist condition that favor denitrification throughout most of the year.

In 4 out of 6 comparison periods we have observed the typical short-lived increase of N_2O emissions after mineral N applications as reported in many studies (e.g. Clayton et al., 1997; Leahy et al., 2004; Jones et al., 2007). Largest fluxes were observed in May and July 2007 and June 2008, when the average WFPS ranged between 72 and 84 % (Table 1). An optimum level for maximum N_2O emission was suggested to be around 65 % (Davidson, 1991), 75 %, (Flechard et al., 2007), 80–85 % (Dobbie et al., 1999; Skiba and Smith, 2000) or 85 % (Ruser et al., 1998). Although the WFPS was highest in March 2007 (85 %), fluxes were relatively small during this period, probably due to the low average temperature of 5.6 °C. This temperature is close to the critical temperature of 5 °C, below which nitrification and denitrification rates have been shown to be negligible in temperate grasslands (Vinther, 1990). In June 2003 and May 2008, where WFPS was on average lowest (66 % and 68 %) compared with other comparison periods (Table 1), N_2O fluxes were always close to background level. It is possible that these two periods were too dry, and mineral N from fertilizer input was taken up by plants directly instead of being nitrified and subsequently denitrified.

No significant relationships were observed between N_2O fluxes, soil water content and soil temperature for either flux measurement methods when investigating all data points per comparison period. This is likely to be due to the competing influences of soil water content, soil temperature and the changing availability of N on microbial processes. Soil moisture as well as soil temperatures were relatively stable

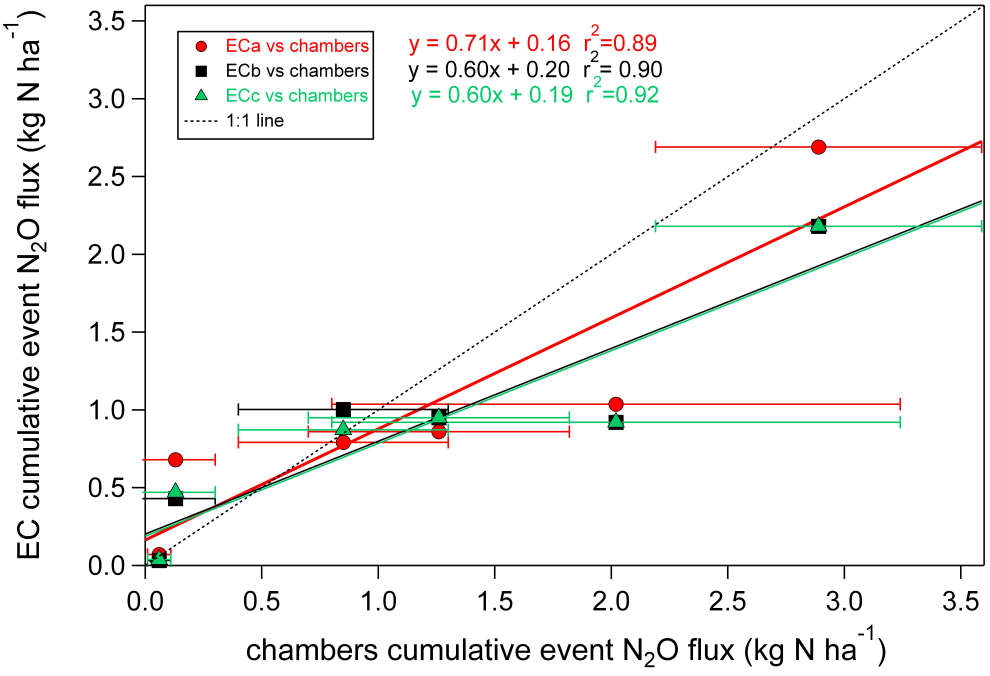

Fig. 4. Comparison of cumulative fluxes from gap-filled data from static chambers and EC, using either comparison points (EC^a), daily averages (EC^b) or 30 min values (EC^c).

throughout each comparison period (CVs ranged between 1.7 and 9.7 %, for soil moisture and 4.6 to 22.3 % for soil temperature). In contrast, mineral N in the soil was generally larger after N application and smaller towards the end of each comparison period, while N from urine and dung patches from grazing animals was likely to have varied over space and time. A positive correlation between N_2O fluxes measured by chambers with NO_3^- in the 0–5c m soil layer is seen when considering data from all comparison ($r^2 = 0.80$).

4.2 Negative N_2O fluxes measured by EC and chamber method

Uptake of N_2O in soils has been reported for grasslands in several studies (e.g. Ryden, 1981; Flechard et al., 2005; Neftel et al., 2007, 2010). It is generally assumed that N_2O uptake is a microbial process in which denitrifiers use N_2O as an electron acceptor for respiration, when oxygen is limited in wet, poorly aerated soils (Bremner, 1997). However, N_2O uptake has also been measured under dry conditions, as oxygen limited sites can develop in well aerated soils inside anaerobic microsites (Hojberg at al., 1994). Denitrifiers are able to use NO_3^-, NO_2^-, and NO as electron acceptors under anaerobic conditions and complete denitrification (reduction of N_2O to N_2) is thought to occur predominantly when N_2O is the only remaining electron acceptor. High NO_3^- concentrations are therefore expected to suppress N_2O uptake. In fact, many authors have reported links between low NO_3^- concentrations and net N_2O uptake on grasslands (e.g. Ryden, 1981; Clayton et al., 1997; Flechard et al., 2005). The flux data presented in this study were all measured immediately after N application and high N_2O uptake was therefore not anticipated. Indeed chamber measurements only showed occasional N_2O uptake at the end of comparison periods when N_2O fluxes were at background levels and NO_3^- concentrations are assumed to be low. Also Clayton et al. (1997) reported occasional N_2O uptake by a fertilized grassland in intervals between fertilizer applications. In July 2007 at Easter Bush the same pattern of N_2O uptake was observed by both chamber and EC measurements. However, chamber measured fluxes were never above detection limit. For all other comparison periods, especially in 2003 and 2008, we measured negative fluxes by EC even shortly after N application. The magnitude of the negative fluxes measured in our study was at times larger than maximum negative values reported in the literature for grasslands (Chapuis-Lardy et al., 2006). For the EC data, the quality control criteria (see Methods section) removed a substantial amount of negative fluxes; although we are critical towards the highly negative fluxes based on the current knowledge of biological soil processes, we could not find a reason to reject those negative flux values without biasing the dataset. It has to be pointed out that until novel chemical analysers will allow less noise in the concentration measurements, the detection of small fluxes is a great challenge. The flux detection limits do not allow the resolution of uptake processes as they are described in controlled experiments; however, when averaging over long terms to get N_2O emissions, that noise tends to be cancelled.

4.3 Spatial and temporal variability

In order to compare the temporal and spatial variability of N_2O fluxes measured by each method, coefficients of variation (CVs) were calculated over each comparison period (Table 2). CVs for chamber and EC measurements represent a combination of spatial and temporal variability. The observation that CVs of chamber measurements were higher than those from EC comparison points reflects the small scale spatial variability detected by the chambers. The high spatial variability of N_2O fluxes at Easter Bush is highlighted by the high coefficients of variation of up to 139 % and by the range of more than 300 ng N_2O-N m^{-2} s^{-1} measured by 4 chambers within the same hour. Hotspots of high N_2O emissions are driven by increased N input through animal urine and dung, and have been measured in fertilized and especially in grazed grasslands (Velthof et al., 1996; Skiba et al., 1998; Flechard et al., 2007). The spatial variability is due to fluctuations in mineral N content, oxygen levels and microbial communities within the soil. The varying N level is caused by a combination of fertilizer N application, the distribution of urine and dung patches, N uptake by the grass roots and microbial biomass and N losses by leaching, denitrification and volatilization (e.g. Velthof, 1995), while the oxygen level depends on the level of soil respiration, soil density and water content, all of which affect the formation of anaerobic zones (Ruser et al., 2006).

The variation in N_2O fluxes by EC measured every 30 min was comparable to the chamber measurements. The variability that the datasets reflect are both spatial and temporal, but there are several factors favouring one or the other technique. Chamber measurements were only conducted once per day and therefore cannot represent short time scale events, such as large emission peaks, which are captured by EC.

The higher CV for EC^c compared to EC^a reflects the additional diurnal variability of N_2O fluxes. However, when looking at the diurnal variation in detail we never observed a clear cycle with a maximum during the day and minimum during the night; neither did we find a correlation of N_2O fluxes with soil temperature. This is in contrast to other studies (e.g. Du et al., 2006) and even to measurements taken on the same field in 2002, where clear diurnal cycles were measured with the same EC setup (Di Marco et al., 2004). This might be due to the lack of a pronounced soil temperature variation specific to the presented comparison periods.

4.4 Comparison of chamber and EC flux measurements during chamber closure

In our study nearly 70 % of N_2O fluxes measured by EC at the time of chamber closure were within the range of chamber measurements over all comparison periods. This is comparable with previous studies where Laville et al. (1997, 1999) and Christensen et al. (1996) found a reasonable agreement between N_2O fluxes measured by EC and chamber methods. Laville et al. (1997 and 1999) compared fluxes over a period of 10 days, using 16 (1997) or 30 (1999) chambers for the comparison and fluxes were measured from bare fertilised soil and irrigated fertilised maize, respectively, while Christensen et al. (1996) compared fluxes over a period of 9 days using 32 chambers from unfertilised arable cropland. In 59 % of all measurements in our study, chamber fluxes were higher than EC comparison points. EC fluxes ranged from 38 % (March 2007) to 225 % (July 2007, after removal of outlier) of chamber measurements; considering all points of comparison, EC fluxes were 70 % of chamber fluxes. In comparative experiments published by Smith et al. (1994) and Pilhatie et al. (2005) N_2O flux values measured with EC were consistently lower than those from chamber methods. Smith et al. (1994 and 1998) measured fluxes over a period of 2 days from agricultural, fertilised grassland using 24 chambers while Pihlatie et al. (2005) presented a comparison period of 6 days from a beech forest using 35 chambers. As we measured fluxes over several periods of 3 to 29 days over several years, our study represents the longest intercomparison to date, spanning a large range of conditions. There are several reasons for the inconsistency observed on the same experimental field during different comparison periods in our study. It needs to be considered that the area which influences the EC measurement (flux footprint) might not always include the position of all the chambers, but only some of them. In Fig. 3 the different shades of symbols indicate the contribution of the area in which the chambers were situated to the footprint of the EC measurement according to this model (open circles = 0–25 %, medium grey = 26–50 %, dark grey = 51–75 %). This footprint analysis showed that the four chosen chambers (for 2007/2008) were in an area with a contribution to the measured flux ranging from 3.7 to 61.2 %. The disagreement of chamber and EC measurements might partly be explained by the potential for large-scale variability across the field, coupled with the fact that the area covered by the four chambers used for the comparison did not always dominate the EC flux measurement; thus, chambers and EC measurements were dominated by different parts of the field. Furthermore, even when the chambers are within the fetch of the EC method, the different techniques integrate fluxes over different spatial scales (e.g. Smith et al., 1994). The different averaging areas challenge a strict comparison of fluxes. As discussed above, it has been shown that N_2O fluxes from soils have a high spatial variability, especially for grazed grasslands. High fluxes measured by chambers most likely represent hotspots, which in the EC approach are integrated alongside low emission areas.

4.5 Cumulative fluxes

Estimates of annual N_2O fluxes are mainly based on measurements from manual chambers taken during daytime which are used as mean daily flux estimates to calculate cumulative fluxes (e.g. Clayton et al., 1997; Jones et al., 2007). However, cumulative annual fluxes calculated from a single

measurement during the day could be biased by missing peak emission periods as well as ignoring possible diurnal pattern. Diurnal patterns of N_2O fluxes after fertiliser applications usually have shown peak fluxes around midday in several studies (e.g. Di Marco et al., 2004; Flechard et al., 2005; Du et al., 2006). In order to examine if the magnitude of cumulative fluxes is biased due to one single sampling at midday, we compared cumulative fluxes calculated from EC daily means (EC^b) with cumulative fluxes calculated from EC comparison points (EC^a), which were taken simultaneously as chamber measurements, usually between 10:00 and 12:00 am. Over all comparison periods, cumulative fluxes from EC^a were actually 117 % of EC^b: this would translate in an overestimation of the cumulative flux when using only central hours of the day values compared to all values through the day. Although there was no clear diurnal pattern in our EC N_2O fluxes, late-morning fluxes were evidently larger than daily averages. The lack of a diurnal cycle in our study prevents the introduction of a correction factor to account for diurnal variability if cumulative fluxes are calculated based on one singular measurement obtained by manual chambers. However, missed short timescale events will still introduce an error leading to potential over or underestimation.

Cumulative fluxes derived from non-gap-filled chamber measurement data are smaller (84 %) than the ones derived from gap-filled data. This shows that the integration method can introduce a bias in the estimate of cumulative fluxes and therefore emission factors. In theory the arithmetic mean of a flux dataset provides an actual integration over time. However, if large fluxes are measured only for a short term, e.g. after N applications, peak values may be over represented, leading to a biased cumulative flux. Indeed chambers data from our comparison periods showed a positively skewed distribution due to large flux values immediately after N application, with the exception of June 2003, where the data distribution was negatively skewed due to large negative fluxes. EC fluxes overall led to smaller cumulative estimates when compared to chambers, but the values were actually higher in the lower range of emission, and lower in the higher range. A possible explanation for the high-end of the emission range would be the sampling of hot spots of emissions by chambers that get smoothed by the EC integration over a larger surface.

Different measurement techniques used on the same field at the same time, lead to emission factor estimates that can be considerably different: if we take for example the data set from March 2007, we find that EFs from EC and chambers would differ by more than a factor 2, and using the same technique but different integrating protocols (EC^c, EC^a) leads to a difference of more than 10 %. Therefore we think it would be advisable to have a common protocol for integrating cumulative fluxes for whichever method is used to assess the cumulative fluxes, to reduce the uncertainty of IPCC emission factors.

5 Conclusions

In this study, N_2O EC fluxes were mostly (70 % of the time) within the range of chamber fluxes. During different comparison periods, EC measured either larger or smaller fluxes compared to the average flux derived from the chambers. One reason for this inconsistency observed on the same experimental field during different comparison periods is partly explained by the possibility that the chosen chambers were not always within the footprint of the EC measurement and therefore measured a different part of the field. The EC method integrates fluxes over a much larger area (0.01–1 km^2) than chambers (<2 m^2, all together). High fluxes measured by chambers can represent hotspots, which do not show in the integrative approach of the EC method. Conversely, the EC flux may include large emissions from specific areas where no chambers are sited. The information given by an EC dataset allows a detailed description of the behaviour of a field as a source or sink for N_2O, as it provides high time resolution measurements, showing short time scale events as well as longer ones. However, the current detection limits of the EC fluxes prevent a complete understanding of the soil uptake processes at the field scale. We recommend therefore that the two methods are used in a complementary fashion, to gather overall emission from EC, and spatial knowledge from chambers: for these, high spatial replication would assess the heterogeneity of the N_2O source. Diurnal variability can be established either by micrometeorological measurements or by the use of autochambers, sampling several times a day when wanting to investigate exchange processes in more detail.

The errors in the estimates of emission factors reflect the uncertainties occurring at different levels:

1. the measurement level: different techniques, or often same technique but following different measurement protocols
2. data quality control level: different standards are used, leading to qualitatively different information following different rejection criteria
3. data analysis level: averaging protocols over the data, leading to different cumulative fluxes.

For these reasons, we think it is paramount at this stage to assess defined protocols in the scientific community, to reduce the uncertainty on emission factors and estimates of national and global N_2O emission inventories.

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