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

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Managed grasslands are known to be an important source of N_2O with estimated global losses of $2.5 \text{ Tg N}_2\text{O-N yr}^{-1}$. Chambers are the most widely used method to measure N_2O fluxes, but also micrometeorological methods have successfully been 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) methods 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 after mineral N application was observed, returning to background level within 2–6 days. Highest fluxes were measured by both methods in July 2007 with maximum values of $1300 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$ (EC) and $651 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$ (chamber method). Frequently, negative fluxes above the detection limit were observed in all comparison periods by EC, while with chambers negative fluxes were always below detection limit. Despite observed negative fluxes, 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. Differences between N_2O fluxes calculated from chamber measurements and EC over the same measurement period were never significant. Overall, N_2O fluxes measured by EC during the time of chamber closure were smaller compared to those measured by chambers, however this was the case in only 3 out of 6 comparison periods. This inconsistency observed on the same experimental field at different times can partly be explained by the fact that the different techniques integrate fluxes over different spatial scales. Large fluxes measured by chambers may have represented local hotspots, which made a small contribution to the flux derived by the EC method which integrates fluxes 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

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of soil temperature. Calculations of cumulative fluxes showed that different integration methods can introduce a large bias in the estimation of cumulative fluxes and therefore emission factors.

1 Introduction

5 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 $N_2O\text{-N}\text{ y}^{-1}$ (65% of total global emissions), 1 Tg of which originate from temperate grasslands (IPCC, 2001a). 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
10 (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 temper-
15 ate climates N_2O emissions have been shown to be largely event driven with rainfall and nitrogen fertilisation being critical factors (e.g. Flechard et al., 2005; 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;
20 Dejardins, 2004).

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). Static chambers are fairly inexpensive, do not require power and are simple to operate. They provide valuable information comparing different treatments or assessing the spatial variability (e.g. Clayton et al., 1994; Jones et al., 2007; Velthof et al., 1996). However, their coverage is limited over space and time. The cover area per measurement is
25

usually less than 1 m² 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 e.g. rainfall, fertilization, rewetting dry soil and freeze-thaw events. It is therefore not surprising that the uncertainty of annual flux estimates from chamber 5 measurements 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 may temporarily change C and N cycling by disturbing the soil and cutting roots, and they might modify the environmental conditions (wind, temperature) during the measurement (e.g. Ambus and Christensen, 1994; Davidson et 10 al., 2002), and their presence in the field may affect the grazing behaviour of animals.

An alternative, non-disruptive approach measuring fluxes at high time resolution and at the field scale level is offered by micrometeorological techniques. These methods require high frequency measurements of meteorological parameters and gas concentrations at some height above the soil-vegetation surface, using high sensitivity gas 15 analysers. The area over which a flux can be integrated by micrometeorological technique ranges from 0.01–1 km⁻², depending on the height of the sampling tower. However, this requires a uniform source surface, which in many agricultural ecosystems may be a limitation. Further downsides of micrometeorological techniques applied to N₂O are that they are expensive and require high expertise. The most widely used micrometeorological technique for N₂O flux measurements is the eddy covariance (EC) 20 method, which relies on the measurement of variations in vertical wind velocity and trace gas concentration above the source surface with high time resolution. N₂O has been measured successfully in agricultural ecosystems by EC since the development of suitable high frequency fast response N₂O analysers, fitted with tunable diode lasers and, more recently, quantum cascade laser (e.g. Wienhold et al., 1995; Di Marco et al., 25 2004; Neftel et al., 2007; Kroon et al., 2010).

In future it is likely that both methods will be used to collect N₂O flux data sets, which will be used to define IPCC EFs. To reduce the uncertainty of estimates their comparability needs to be investigated. In this paper we present a comparison of N₂O

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flux data sets measured by 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. Flux ranges as well as cumulative fluxes per comparison period are presented and possible reasons for differences in ranges and the influence of using different temporal integrating methods on cumulative fluxes are discussed.

2 Materials and methods

2.1 Site description

10 The measurement site, Easter Bush, is located in a rural area, 10 km south of Edinburgh, Scotland ($3^{\circ}12'W$, $55^{\circ}52'N$, elevation 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” field (Fig. 1). The measurement equipment for the eddy covariance measurements was situated on the boundary between the two fields. This enabled eddy covariance flux measurements from the South field in SW wind direction and from the North field in NE wind direction, the two prevailing wind directions (e.g. Milford et al., 2001). Over the periods 2003–2008, the fields received mineral fertiliser of an average $183\text{ kg N ha}^{-1}\text{ yr}^{-1}$ split into three to four fertiliser applications per year. Comparison measurements between EC and chamber methods of N_2O fluxes were made at fertilisation events on six occasions; in 2003, 2007 and 2008 (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 live stock 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

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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 H₂O) 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.

2.2 Chamber measurements of N₂O fluxes

Static chambers, each covering an area of 0.1256 m², 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 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 N₂O using a Hewlett Packard 5890 series II gas chromatograph (Agilent Technologies, Stockport, UK), fitted with an electron capture detector (detection limit: N₂O < 0.2 μl l⁻¹ (ppmV)). Chamber closure and gas sampling were carried out between 10:00 h and 12:00 h. Fluxes were calculated as,

$$F = (\Delta C) / (\Delta t) \cdot (V/A) \quad (1)$$

where V and A are the volume and surface area of the chamber, ΔC is the difference in the N₂O concentration from the start and end gas sample and Δt is the closing time, whereas $\Delta C / \Delta t$ is the slope of the gas concentration change with time. Linearity tests 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 detection limit for N₂O fluxes measured by the chambers in this campaign was estimated as 12 ng N₂O-N m⁻² s⁻¹.
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Eddy-covariance measurements of N₂O fluxes

The eddy covariance flux was calculated as the covariance between the N₂O concentration (χ) and the vertical component of the wind speed (w) as:

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

5 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

10 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 N₂O (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 N₂O concentration was measured by a TDL (Aerodyne Research Inc., Billerica, MA, US) located in a monitoring cabin on the field. An inlet line of Dekabon[®] tubing, 1/4" OD was placed

15 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 N₂O 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

20 estimated to be 1 ppbV.

25 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

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hour period. 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). For a 30 min averaging period the detection limit of the N_2O flux measurement was estimated at $11 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$: a zero-flux was measured from zero- N_2O air flushed through the system. Rejection of N_2O fluxes due to quality control (bad wind sector, extreme low turbulence, stability of the laser source, electronic noise) resulted in a data coverage for the EC fluxes of 69% in June 2003, 60% in March 2007, 62% in May 2007, 65% in June 2007, 18% in May 2008 and 25% in July 2008.

2.3 Additional measurements

15 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^-)
 20 was determined in samples collected at two depths (0–5 cm and 5–15 cm) and sam-
 ples were frozen at -16°C until analysis. Soil mineral N contents 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).

2.4 Statistical analysis and calculation of cumulative fluxes

Eddy covariance fluxes were calculated for every half hour, while chamber fluxes were measured once a day over a one hour period (between 10:00 and 12:00, although data were not collected every day). To compare fluxes measured by both methods,

5 EC fluxes were calculated for the period of chamber closure by averaging appropriate 30 min fluxes. These data are referred to as EC comparison points throughout the manuscript (EC^a). The chambers used for these comparison points (14 chambers in the South field in 2003 and 4 chambers from either South or North field in 2007 and 2008) were chosen by wind sector selection. A footprint analysis was undertaken using the approach reported by Neftel et al. (2008) for data in 2007 and 2008, which calculated the probability of all four chambers being within the EC footprint. To compare chambers and EC comparison points an orthogonal regression analysis was performed. Cumulative N₂O fluxes were calculated over each comparison period using different averaging intervals. (1) Hourly measurements from chambers and EC comparison points (EC^a) were used as daily averages for cumulative flux calculations. (2) EC half hourly values were averaged over daily periods (EC^b). (3) Half hourly EC data were averaged over all days of each comparison period (EC^c) (see Tables 2 and 3). The significance of differences between mean and median fluxes was tested by performing a t-Test (GenStat, 12th Edition). Cumulative fluxes were calculated with and without gap-filling. When derived from non gap-filled data, the cumulative flux was calculated by averaging all data and multiplying the average by the number of time steps (either 30 min or days). 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. For the calculation of cumulative fluxes using gap-filled data, linear interpolation was used for chambers and EC comparison points. Gap-filled data were then summed up per comparison period.

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3 Results

The length of the different comparison periods varied between 3 and 29 days and the rate of N applications varied between 48 and 69 kg N ha^{-1} per period (Table 1). The comparison periods cover a range of environmental conditions, which is reflected in 5 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 a water filled pore space (WFPS) of 65%, 66% and 87%, respectively. Average soil temperatures per comparison period ranged from 10 5.6 °C (March 2007) to 14.0 °C (July 2007) (Table 1).

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 emissions after the N application was observed in all comparison periods in 2007 and in June 2008 by both methods and in May 2008 15 only by the chamber method (Fig. 2). Fluxes declined to background levels (here defined as average daily flux below 50 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$) after 2 to 6 days. No response in N_2O emissions to fertilizer input was observed in June 2003 by both methods and in May 2008 by the EC method. Highest fluxes were measured by both methods in July 2007, with maximum values of 1300 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$ measured by EC on 20 14 July and 651 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$ measured by the chamber method on 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%, which corresponds to a WFPS of 83%. In June 2003 and May 2008 fluxes were generally small with maximum values 25 reaching 97.3 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$ measured by EC and 91 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$ measured by chamber methods in 2003, while corresponding values in May 2008 were 134.2 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$ and 87.7 ng $\text{N}_2\text{O-N m}^{-2} \text{s}^{-1}$. During both these periods soil conditions

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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 comparison periods by EC while by chamber methods negative fluxes were not seen in June 2003 and July 2007. N_2O uptake was observed in 10% of all EC data (30 min data) (ranging from 6–42%, depending on comparison period), and 4.4% of all chamber measurements. Largest negative values were measured in 2003 with up to $-141 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$ by EC, whereas with the chamber method largest negative fluxes of only $-3.1 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$ were measured in March 2007. For EC data 78% of all measured negative fluxes were above detection limit, while for chamber measurements negative fluxes were always below the detection limit. 70% of all negative fluxes measured by EC occurred during daytime (between 08:00–20:00).

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 $385 \text{ ng N}_2\text{O m}^{-2} \text{ s}^{-1}$, compared to an average variation of $111 \text{ ng N}_2\text{O m}^{-2} \text{ s}^{-1}$ 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 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; 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 smallest N_2O fluxes were measured by the EC technique in June 2003 ($-141 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$) and the largest in July 2007 ($+1303 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$), (Table 2). However, half the measurements, between the 25th and 75th percentile, were found to lie within a narrow range between -27.4 and $252.0 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$. Despite the observed negative fluxes, median and average fluxes over each period were always positive. Median N_2O fluxes per comparison period ranged

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from 12.0 to 97 ng N₂O-N m⁻² s⁻¹ for chamber methods, from 32.8 to 116.5 ng N₂O-N m⁻² s⁻¹ for EC comparison points, from 10.7 to 49.1 ng N₂O-N m⁻² s⁻¹ for EC daily average fluxes and from 22.7 to 57.7 ng N₂O-N m⁻² s⁻¹ for all EC 30 min data. Mean fluxes were on average 1.4 times larger than median fluxes, indicating that fluxes were not normally distributed. Differences between mean as well as median N₂O fluxes calculated from chamber measurements and EC comparison points per comparison period were never significant ($p < 0.05$, T-test), with p-values ranging from 0.06–0.82.

Variability of N₂O fluxes was expressed as coefficient of variation (CV, defined here as $\text{stdev}/\text{mean} \times 100$) and calculated for both techniques and different averaging methods for EC over each comparison period. Values of the CV of chamber measurements were always higher than from EC comparison points, and the highest variability was measured in March 2007 at 139.3%. The variation of N₂O fluxes was generally higher in the EC 30 min data compared to the chamber measurements with the highest CV observed in June 2003 at 415.9%. However, in March 2007 the variability was higher in chambers compared to EC 30 min measurements.

3.2 Comparison of chamber and EC comparison points

The range of N₂O fluxes measured on the same day varied widely between the 4 chambers. It was largest on 15 March 2007, at 338 ng N₂O-N m⁻² s⁻¹, immediately after fertilizer application and smallest on 10 May 2007, at 2 ng N₂O-N m⁻² s⁻¹, five days before fertilizer application. EC comparison points were within the range of the chamber measurements in 69% of all measurements over the 6 comparison periods (ranging from 25% in May 2008 to 100% in June 2003).

Scatter-plots showing orthogonal regression between EC and chamber measurements made during the same hour (EC^a) are shown in Fig. 3 for all periods. The number of comparison points per period varied from 3 (June 2003) to 11 (June 2007). In five out of six comparison periods there was a positive correlation between values from both methods, while in May 2008 the correlation was negative. In June 2003

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and May 2008 EC fluxes were higher compared to chamber measurements. For all other comparison periods, it was the opposite, with EC values being 28% ($r^2 = 0.42$), 32% ($r^2 = 0.84$), 71% ($r^2 = 0.31$) and 49% ($r^2 = 0.34$) of measurements made by corresponding chamber measurements for March, May and June 2007 and July 2008, respectively. The elimination of one outlier in June 2007 resulted in the EC values being larger than the chamber values, with EC being 199% ($r^2 = 0.93$) of chamber measurements. The removal of one outlier in May 2008 increased r^2 from 0.61 to 0.92 while the elimination of two outliers in June 2008 increased r^2 from 0.34 to 0.73. Fluxes from chambers were higher than EC fluxes in 59% of cases.

10 3.3 Cumulative fluxes

Cumulative fluxes were calculated for each comparison period for data obtained by chamber and EC method (Table 3). 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 values and therefore potentially on emission factors, we calculated cumulative N_2O fluxes by both frequently used integration methods. For chamber measurements, using non gap-filled data lead to larger cumulative fluxes in 4 out of the 6 comparison periods, whereas differences induced by the integration method ranged from 0% (June 2003) to 48% (May 2008). For EC measurements differences induced by the integration method ranged from 0% (June 2003, EC^a) to 50% (June 2003, EC^c). Overall 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 ($r^2 = 0.99$), 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.

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Cumulative fluxes from chambers were larger than EC^a fluxes in 2007 and June 2008 (up to 1.9 times), when using gap-filled data, whereas the opposite was found for the other periods. Cumulative EC^a fluxes represented 72% of chamber fluxes ($r^2 = 0.81$) when using gap-filled data.

5 Cumulative fluxes calculated from EC^a were always larger than from EC^b except for March 2007, and EC^a cumulative fluxes were 144% of EC^b cumulative fluxes ($r^2 = 0.97$), when using gap-filled data. Cumulative fluxes calculated from EC^c were higher compared to cumulative fluxes calculated from EC^b during all comparison periods with the exception of June 2003.

10 4 Discussion

There are uncertainties in both chamber and EC approaches. As mentioned above, micro-climate and turbulence may be slightly altered within a chamber and their small footprint makes them very sensitive to local soil conditions. An important additional uncertainty for chamber measurements in grazed and fertilized grassland systems is their effect on grazing behavior in and around the chamber, and the statistical variability in the fertilizer application across the field. Similarly, eddy-covariance measurements are subject to various artefacts: flux losses can arise e.g. from inadequate 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). By contrast, it has more recently been realized that the determination of the time-lag between the measurements of turbulence and N₂O 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

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are very close because the statistical variability averages out (e.g. Dämmgen et al., 2005; Nemitz et al., 2009). These uncertainties need to be borne in mind when interpreting the measurement results.

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

5 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 range 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
10 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 heterotrophic denitrifiers and by simulating 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
15 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 four out of six 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 83%. 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 (87%), 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
25

to be negligible (Vinther, 1990). In June 2003 and May 2008, where WFPS was on average lowest (65 and 66%) compared with other comparison periods, 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 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 0–5 cm soil layer could be seen if data from all comparison periods were considered ($r^2 = 0.80$).

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 et 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^-

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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, negative EC fluxes were mostly above detection limit, whereas the 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. In some instances, the laser source instability is affecting the concentration measurements, creating variations that do not reflect the real atmospheric turbulence (see also Di Marco, 2005): in order to avoid instrumental artifacts, we applied 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. The magnitude of the negative fluxes measured in our study were frequently larger than maximum negative values (up to $-69 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$) reported in the literature for grasslands (Chapuis-Lardy et al., 2006). 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.

4.3 Spatial and temporal variability

In order to compare the temporal and spatial variability of N_2O fluxes measured by each method, coefficient of variations (CVs) were calculated over each comparison

period (Table 2). CVs for chamber measurements represent a combination of spatial and temporal variability while CVs for EC measurements represent temporal variability only. The observation that CVs of chamber measurements were higher than those from EC comparison points demonstrates the spatial variability of chamber measurements.

5 The high spatial variability is highlighted by the high coefficients of variation of up to 139% and by the range of more than $300 \text{ ng N}_2\text{O-N m}^{-2} \text{ s}^{-1}$ 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 10 spatial variability is due to fluctuations in mineral N content and oxygen levels 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 15 content all of which affect the formation of anaerobic zones (Ruser et al., 2006).

Despite the above-discussed high spatial variability, the variation in N_2O fluxes over each comparison period was generally higher with the EC 30 min data compared to the chamber measurements. This has several reasons; chamber measurements were only conducted once per day and therefore have a larger probability of missing big 20 emission peaks. High variations in EC fluxes also result from the fact that each EC value is a single measurement point and therefore has a higher statistical uncertainty. For example, Nemitz et al. (2009) demonstrated that measurements with several EC systems above the same grassland differed by typically 20% for fluxes that could be measured with an ultrasonic anemometer alone (momentum, sensible heat), owing to 25 statistical variability in the turbulence. The TDL required for N_2O is expected to add further uncertainty. Indeed, variability was largest in June 2003 where EC measured numerous large negative fluxes pointing to a more variable performance of the N_2O analyser during this time. These large negative EC fluxes could at times be due to artifacts, as discussed above (see Sect. 4.2), and could potentially be smoothed out

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using a second EC system. However, due to the cost of the instruments this is almost never practiced. In March 2007 the variability of chamber flux measurements was larger than EC (30 min) flux measurements. This was due to the exceptionally high spatial variability in chamber measurements on 15 and 16 March caused by large fluxes in one chamber, possibly due to dung or urine deposition by a grazing sheep in the specific chamber.

The higher CV for EC^c compared to EC^a reflects the additional diurnal variability of N₂O 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 N₂O 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.

15 4.4 Comparison of chamber and EC flux measurements

In our study nearly 70% of N₂O 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 N₂O fluxes measured by EC and chamber methods. Laville et al. 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. 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, while in only 3 out of 6 comparison periods the EC method measured lower fluxes compared to the average of all chambers, if outliers were removed. EC fluxes ranged from 42% (May 2007) to 205% (June 2008) of chamber measurements, falling almost within a factor of 2. In comparative experiments published by

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4.5 Cumulative fluxes

Estimates of annual N_2O fluxes are mainly based on measurements from manual chambers taken around midday 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, which were taken between 10:00 and 12:00. Averaged over all comparison periods, cumulative fluxes from EC^a were actually by 44% larger than from EC^b . Although there was no clear diurnal pattern in the EC N_2O flux, late-morning fluxes were evidently nevertheless 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 time-scale events will still introduce an error leading to potential over or underestimation.

Comparisons of cumulative fluxes calculated by either using gap-filled or non gap-filled data showed a difference of up to 48% per comparison period. This shows that the integration method can introduce a large bias in the estimation 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 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

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large negative fluxes. It is therefore advisable to split fluxes into “trigger flux events” and “back-ground fluxes” as suggested by Flechard et al. (2007) in order to reduce the bias from the integration method. Furthermore, it would be advisable to have a common protocol for integrating cumulative fluxes to reduce the uncertainty of IPCC emission factors.

5

5 Conclusions

We have shown that there was a reasonable agreement between N_2O fluxes measured by chambers and EC given that EC fluxes at the same time were mostly (69%) within the range of chamber measurements, while average chamber values and EC results 10 agreed within a factor of two for 51% of the time. Furthermore, differences between median as well as average N_2O fluxes calculated from chamber measurements and EC comparison points per comparison period were never significant. However, 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 15 on the same experimental field during different comparison periods can partly be explained by the possibility that the chosen chambers were not always within the fetch of the EC measurement and therefore measured a different part of the field. The EC method integrates fluxes over a much larger area ($0.01\text{--}1\text{ km}^2$) than chambers ($<2\text{ m}^2$). High fluxes measured by chambers can represent hotspots, which do 20 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. We recommend that the two methods should be used simultaneously in order to gather spatial knowledge from chambers and overall emission from EC. We recommend to use high spatial replication when sampling by manual chamber methods to account for the heterogeneity of the N_2O source. Diurnal variability needs to be established either by 25 the micrometeorological measurements or by the use of auto-chambers, which sample several times a day, when wanting to investigate exchange processes in more detail.

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The comparison of using either gap-filled or non gap-filled data to calculate cumulative fluxes showed the possibility of a high error introduced by the integration method. We recommend splitting fluxes into “trigger emission event” and “background fluxes”, applying the gap-filled integration method for the first and the non gap-filled integration methods for the latter, in order to reduce the bias from the used integration method. We also suggest the use of a defined protocol for the calculation of cumulative fluxes in order to reduce the uncertainty of emission factors and estimates of national N_2O emission inventories.

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

Comparison period	Duration [d]	Fertilisation date	N fertiliser input [kg N ha^{-1}]	T_{air} [$^{\circ}\text{C}$]	T_{soil} (7.5 cm) [$^{\circ}\text{C}$]	SWC (7.5 cm) [%]	Rain [mm]
11 Jun–13 Jun 2003	3	10 Jun 2003	48	14.9	13.8	35	2
15 Mar–3 Apr 2007	20	14 Mar 2007	69	5.9	5.6	47	53
10 May–7 Jun 2007	29	16 May 2007	51.75	10.3	10.9	41	120
10 Jul–27 Jul 2007	18	11 Jul 2007	51.75	13.5	14.0	45	65
14 May–26 May 2008	13	13 May 2008	51.75	10.5	11.8	36	18
20 Jun–7 Jul 2008	17	18 Jun 2008	51.75	12.4	12.4	39	85



Comparison period	Method	N	N ₂ O flux [ng N ₂ O-N m ⁻² s ⁻¹]							
			no. of values	min	25%	mean	median	75%	max	CV% ^d
11 Jun–13 Jun 2003	chambers (14)	45		0.4	6.9	24.5	17.9	35.4	91.0	108.3
	EC ^a	3		9.0	26.4	39.2	43.9	54.4	64.9	71.9
	EC ^b	3		9.6	10.2	11.0	10.7	11.6	12.5	12.9
	EC ^c	100		-141.1	-27.4	9.3	17.9	42.0	97.3	415.9
15 Mar–3 Apr 2007	chambers (4)	44		-3.1	7.7	56.4	27.3	70.1	359.1	139.3
	EC ^a	11		0.6	23.6	38.6	32.8	57.9	62.7	64.4
	EC ^b	20		13.9	23.6	43.5	33.8	54.5	150.7	73.6
	EC ^c	574		-75.8	19.2	44.3	33.8	57.8	341.3	98.1
10 May–7 Jun 2007	chambers (4)	44		-2.6	7.5	112.3	84.5	153.7	540.5	109.4
	EC ^a	11		-0.8	32.4	51.7	51.6	65.1	115.6	69.4
	EC ^b	29		8.9	18.8	35.5	23.3	36.9	143.1	87.8
	EC ^c	861		-61.4	13.2	41.9	26.2	58.0	281.8	111.7
10 Jul–27 Jul 2007	chambers (4)	32		3.1	45.1	154.9	97.0	207.9	651.2	102.6
	EC ^a	8		13.2	40.1	178.8	116.5	267.0	498.0	100.4
	EC ^b	18		16.0	33.8	131.1	49.1	136.8	707.4	139.2
	EC ^c	554		-92.7	29.1	170.0	57.7	252.0	1303.5	130.8
14 May–26 May 2008	chambers (4)	16		-1.7	1.5	22.6	12.0	30.3	87.8	125.2
	EC ^a	4		32.9	40.9	51.6	44.0	54.7	82.6	45.1
	EC ^b	13		6.6	12.9	27.7	17.1	26.7	94.1	89.6
	EC ^c	111		-84.6	4.8	31.2	34.9	59.1	134.2	150.9
20 Jun–7 Jul 2008	chambers (4)	32		-0.18	14.2	69.7	56.1	90.0	308.5	104.0
	EC ^a	8		-29.9	39.8	54.9	49.8	72.6	130.6	85.7
	EC ^b	18		0.42	45.6	45.7	48.9	53.9	86.2	38.8
	EC ^c	219		-70.7	25.5	44.1	43.59	66.5	395.8	117.9

^a using only eddy covariance comparison points (between 10:00 h and 12:00 h)

^b using daily averages calculated from eddy covariance 30 min data, missing daily values were gap-filled by linear interpolation

^c using all eddy covariance 30 min data

^d CV%; Coefficient of Variation = $(\text{stddev}/\text{mean}) \times 100$, values represent mean of the CV% over all measurements (30 min values or daily averages)



Table 3. Cumulative N₂O fluxes from chamber and eddy covariance (EC) measurements for all six comparison periods. Fluxes were either calculated using non gap-filled data or gap-filled data by linear interpolation. Values in brackets represent standard deviations from 14 (2003) or 4 (2007/2008) chambers.

Comparison period	Method	Cumulative N ₂ O flux [kg N ha ⁻¹ comparison period ⁻¹]	
		Non-gap-filled data	gap-filled data
11 Jun–13 Jun 2003	chambers	0.06 (±0.05)	0.06 (±0.05)
	EC ^a	0.10	0.10
	EC ^b	0.03	0.03
	EC ^c	0.02	0.03
15 Mar–3 Apr 2007	chambers	0.98 (±0.45)	0.85 (±0.40)
	EC ^a	0.67	0.63
	EC ^b	0.75	0.73
	EC ^c	0.80	0.72
10 May–7 Jun 2007	chambers	2.05 (±1.22)	2.02 (±1.03)
	EC ^a	1.29	1.07
	EC ^b	0.89	0.92
	EC ^c	1.05	0.92
10 Jul–27 Jul 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 May–26 May 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 Jun–7 Jul 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 (between 10:00 h and 12:00 h)

^b using daily averages calculated from eddy covariance 30 min data

^c using all eddy covariance 30 min data

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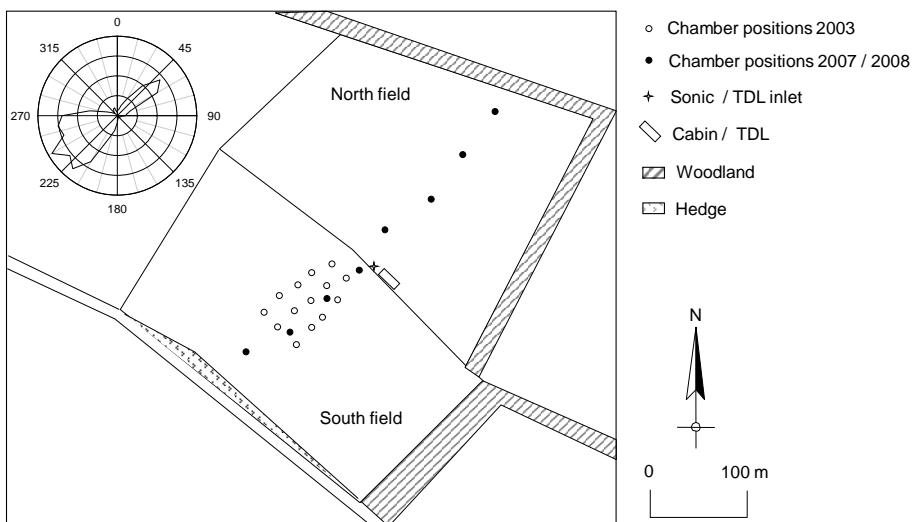


Fig. 1. Site diagram of the study field Easter Bush, showing locations of static chambers in the South and North field in 2003 and 2007/2008, micrometeorological mast (eddy covariance inlet and sonic position) and cabin (containing TDL) on the boundary of the two fields and prevailing wind directions.

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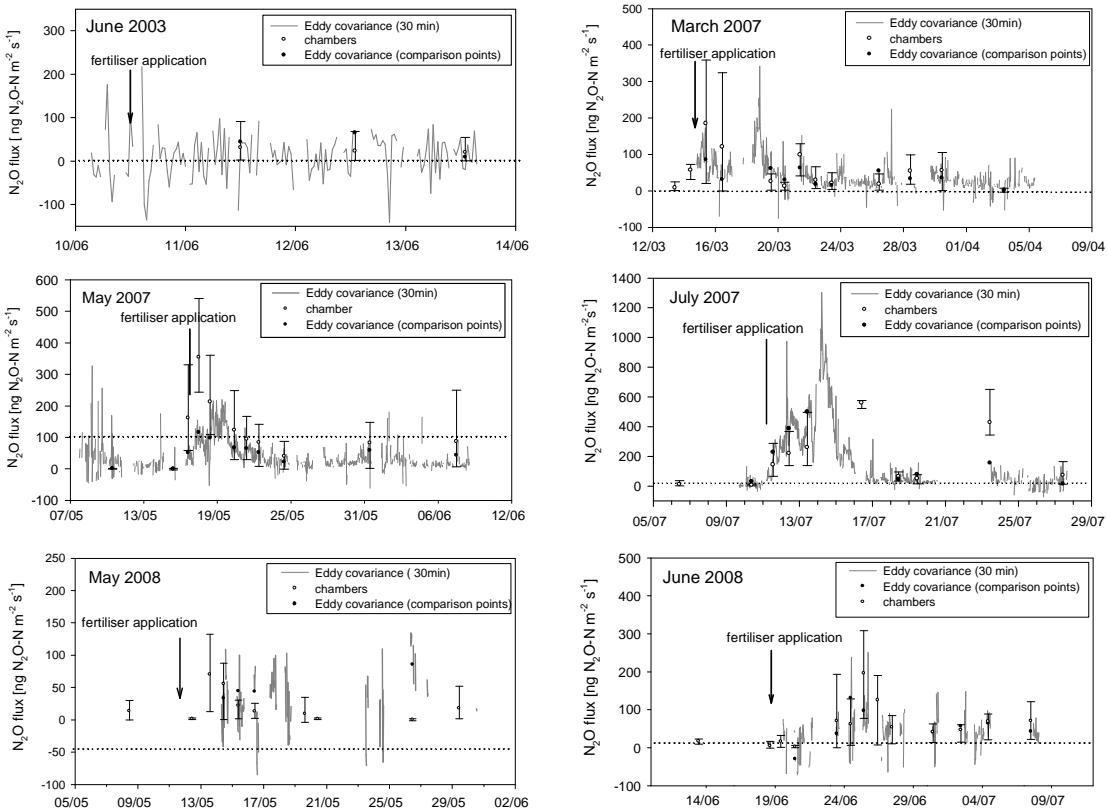


Fig. 2. N_2O fluxes obtained with eddy covariance and static chambers for 6 comparison periods; eddy covariance data are 30 min values (grey line) or values averaged over the one hour period when chambers were closed (between 10:00–12:00, black circles). Chamber measurement points represent the average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

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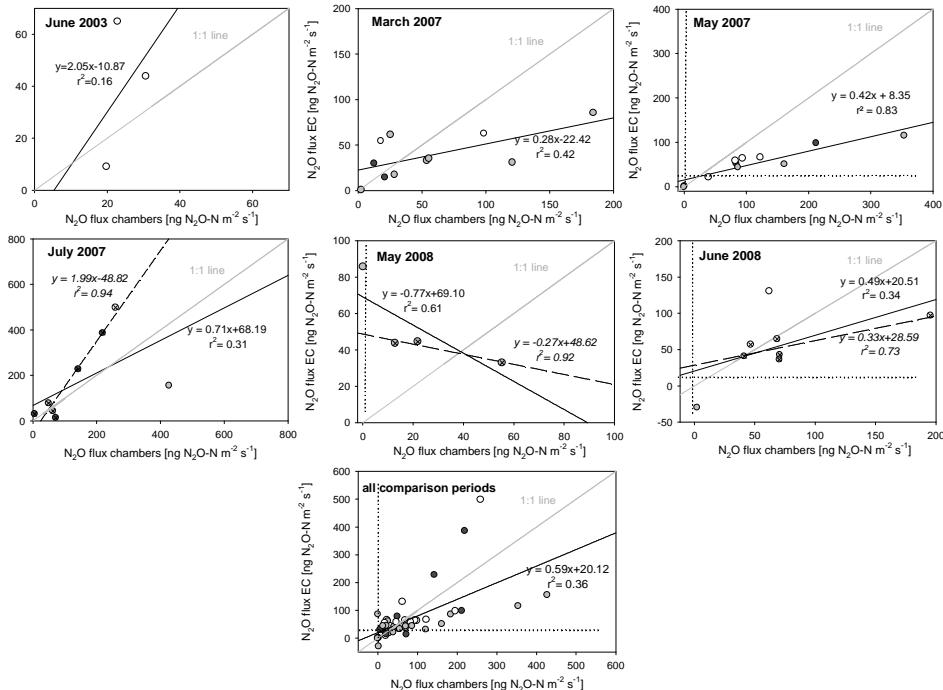


Fig. 3. Comparison of N_2O fluxes obtained at the same hour (between 10:00 and 12:00) with eddy covariance (EC) and static chambers for all 6 comparison periods; June 2003, March 2007, May 2007, June 2007, May 2008, July 2008 and data from all comparison periods. For EC data 30 min values were averaged over the same hour period when chambers were closed. Chamber values represent an average of 14 (2003) or 4 (2007/2008) chambers. Circles represent all comparison points, while crosses represent the 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%).

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