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Published in Nutr Cycl Agroecosyst (2008) 82:175–186

ECN-W--08-055 May 2008

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DOI 10.1007/s10705-008-9179-x

RESEARCH ARTICLE

The importance of reducing the systematic error due to non-linearity in N_2O flux measurements by static chambers

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Received: 31 January 2008 / Accepted: 16 April 2008 / Published online: 14 May 2008

Abstract Closed (non-steady state) chamber measurements are often used to determine the gas exchange of N_2O. Many researchers have addressed the underestimation of the emission estimates obtained from closed chamber measurements when using linear regression methods. However, the linear regression method is still usually applied to derive the flux. The importance of using non-linear regression methods is demonstrated with data from four fertilizing events each consisting of 1 month of automatic chamber measurements at Cabauw in the Netherlands in the period from July 2005 to July 2006. It is presented that the cumulative emission estimates with the exponential regression method are close to the cumulative emissions estimates with the intercept method. The linear estimates differ by up to 60% of the estimates with the exponential method. The performance of each method is validated using a C_2H_6 tracer and a goodness-of-fit analysis. The goodness-of-fit is much better for the exponential than the linear regression method. The systematic error due to linear regression is of the same order as the estimated uncertainty due to temporal variation. Therefore, closed-chamber data should be tested for non-linearity and an appropriate method should be used to calculate the flux.

Keywords Fertilizer management · Grassland · Non-linearity · N_2O flux · Static chamber · Systematic error

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Introduction

The greenhouse gas nitrous oxide (N_2O) plays an important role in global warming with global warming potential 296 times greater than CO_2 for a 100-year time horizon (IPCC 2001). This gas may also contribute to the destruction of stratospheric ozone (Crutzen 1981), which protects the biosphere from harmful levels of ultraviolet radiation. The N_2O fluxes are influenced by soil properties, management practices and weather. The emission of N_2O may be perceived as a leakage of intermediate products of nitrification and denitrification (Hansen et al. 1993). Agricultural soils are major sources of N_2O (IPCC 2006). However, there are significant uncertainties in the estimated N_2O fluxes, mainly owing to a combination of complexity of the source (i.e., spatial and temporal variation), limitations in the measurement equipment and the methodology used to quantify emissions.

Closed (non-steady state) chamber measurements are often used to determine the gas exchange of N_2O (e.g., Gao and Yates 1998; Ruser et al. 1998; Laville

et al. 1999; Pihlatie et al. 2005; Hendriks et al. 2007). A linear regression method is usually used to derive the flux (e.g., Ruser et al. 1998; Laville et al. 1999; Hendriks et al. 2007). However, when a chamber is placed over the soil the concentration gradient within the soil and the atmosphere is altered (e.g., Healy et al. 1996; Conen and Smith 2000). The gas flux is dependent on the concentration gradient and the diffusity of the soil following Fick's first law. Therefore, as the concentration within the chamber headspace increases, the gradient decreases, the flux begins to decline, and the tracing headspace concentration may begin to flatten out (Davidson et al. 2002).

Many researchers have addressed the underestimation of closed chamber measurements due to linear regression methods. The underestimation is shown with real measurements (e.g., Hutchinson and Mosier 1981; Anthony et al. 1995; Pederson et al. 2001; Kutzbach et al. 2007) and models based on the underlying physical processes (e.g., Livingston et al. 2006). In spite of the systematic fault caused by this underestimation, most researchers still use the linear regression method for determining the exchange of N_2O. There can be several reasons for still using linear regression methods. First, linearity is assumed in case of short measurement times. Second, linear regression method is much easier in use than all other methods. Third, the uncertainty due to spatial and temporal variation in N_2O exchanges is assumed to be much larger than the biases due to linear regression.

The importance of using a non-linear regression method is shown in this paper. The intercept method is demonstrated as a good and easy method for determining the fluxes. Near-continuous measurements of N_2O are used of four fertilizing events. A goodness-of-fit analysis and a C_2H_6 tracer are used to validate the accuracy of the linear regression method.

Experimental site and climatic conditions

The near-continuous automatic chamber measurements were performed at a grassland site, which is located near the village Cabauw, in the Netherlands (51°58′12.73″N, 4°55′34.98″E). The soil characteristics for this area were studied by Jager et al. (1976). The following vertical structure was found: 0–0.03 m is the turf zone; 0.03–0.18 m is 35–50% clay and 8–12% is organic matter with high root density; 0.18–0.60 m is 45–55% clay and 1–3% is organic matter with low root density; 0.60–0.75 m is a mixture of clay and peat; 0.75–1.00 m is peat. The dominant grass species are *Lolium perenne* (55%), *Festuca pratense* (15%) and *Phleum pratense* (15%) (Beljaars and Bosveld 1996). The measurement field consists of meadows and narrow ditches which are on average 40 m apart. The water level in the ditches is kept at about 0.40 m below the surface (Beljaars and Bosveld 1996). The grass height ranges from 0.03 to 0.30 m. The average grass dry matter was about 18%. The automatic chamber measurements were performed from July 2005 to July 2006. The same management protocol was applied on the surface of the automatic chamber at Cabauw as on an intensively managed dairy farm at Oukoop. The amount of artificial fertilizer was therefore equal to the applied N at this farm site. Calcium ammonium nitrate (CAN) fertilizer was used which contains 27% N.

This farm located in Oukoop is near the town of Reeuwijk in the Netherlands (52°02′11.22″N, 4°46′49.53″E). Manure and fertilizer were applied about five times a year from February to September, and there were five harvest events. Manure and artificial fertilizer application were about 55 m^3 ha^{-1} $year^{-1}$ (253 kg N ha^{-1} $year^{-1}$) and 320 kg ha^{-1} $year^{-1}$ (84 kg N ha^{-1} $year^{-1}$) in 2006. Fast chamber measurements of N_2O were carried out to investigate among other the effect of sampling frequency and measurement time on the flux estimates. Eddy covariance measurements of CO_2 (Veenendaal et al. 2007), CH_4 and N_2O (Kroon et al. 2007) were near-continuously performed at this location. The climate in both areas is temperate and wet, with an average temperature of 11.3°C in 2006, and with an average annual precipitation of about 870 mm in 2006.

Instrumentation and methodology

Instrumentation

Near-continuous automatic chamber measurements were performed for N_2O using the closed chamber technique. The automatic chamber used in this study had a surface area of 0.49 m^2 and a height of 0.25 m. Thus, the chamber headspace volume was 0.12 m^3

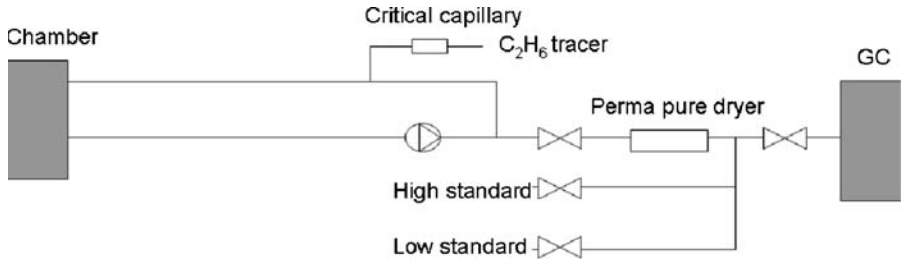

Fig. 1 Schematic representation of the sampling system

(120 l). The chamber had an aluminum steel base which was inserted 0.15 m into the ground. The chamber lids were made from white PVC to minimize heating by direct sunlight. A fan was installed to provide well-mixed air within the headspace. The lid was opened and closed using a 220-V motor controlled by a personal computer.

In this system, the air was circulated from the headspace to the analyzer and returned to the chamber with a flow rate of 5 l min^{-1} (see Fig. 1 for a schematic view). A polyethylene (PE) tube was used of 30 m in length and 6.35 mm (1/4 inch) in diameter. A C_2H_6 tracer of 5,000 ppm was added to the flow at a rate of 1.6 ml min^{-1} for determining the concentration behavior within the chamber headspace.

A gas sample of 2 ml was taken each 5 min from which four measurement samples and one low and high calibration sample were taken during the total enclosure time of 25 min. The measurement samples were taken at 0, 5, 15 and 25 min and the low and high calibration at 10 and 20 min. The calibration gasses were N_2/O_2 mixtures from Scott specialty gasses in the Netherlands (standards are given in Table 1). The measurement samples were dried using a moisture trap (Perma Pure) before analyzing. A gas chromatograph (Interscience Compact GC, The Netherlands) fitted with two detectors was used to determine the concentrations of the N_2O and C_2H_6 samples. The N_2O concentrations were measured using an electron capture detector and the C_2H_6 concentrations using a flame ionization detector. The C_2H_6 concentrations were measured using a 3.175-mm (1/8-inch) Porapak Q column with a length of 2 m and the concentrations of N_2O using a 3.175-mm (1/8-inch) Molsieve 5A column also with a length of 2 m. The temperature of the column oven was 50°C and the flow rate of the carrier gas N_2 was 20 ml min^{-1}. The whole process was controlled using a personal computer with a commercial program Class-VP and a second program developed at ECN. The computer system was available for remote control.

Table 1 Calibration standards used at Cabauw and Oukoop in the Netherlands (Scott specialty gasses, the Netherlands)

Site	Species	Low-standard (ppb)	High-standard (ppb)
Cabauw	C_2H_6	2,000	10,000
	N_2O	300	500
Oukoop	N_2O	300	610

Fast chamber measurements of N_2O were made using a cylindrical static chamber made of non-transparent PVC with a surface area of 0.072 m^2 and a height of 0.20 m. Thus, the chamber headspace volume was equal to 0.01 m^3 (14.4 l). The chambers were attached to PVC frames, which were inserted 0.15 m into the ground. A fan was installed to provide well-mixed air within the chamber space. A closed loop was formed between the chamber and the quantum cascade laser (QCL) spectrometer (model QCLTILDAS-76, Aerodyne Research, Billerica, Mass., USA). A PE tube with a length of 75 m and 6.35 mm (1/4 inch) in diameter was used. The N_2O concentrations were continuously measured with a sampling frequency of 3.5 Hz. Low and high calibrations were frequently performed using a N_2/O_2 mixture from Scott specialty gasses in the Netherlands (standards are given in Table 1). The concentration values and times were saved using the QCL software TDL-Wintel. For more information about the QCL spectrometer set-up the reader is referred to Kroon et al. (2007).

Methodology

The gas concentration within a chamber headspace starts to change when the chamber is placed on the soil. The behavior of the concentration was classified in eight groups related to their concentration rise in the chamber headspace (see Fig. 2). Only the fluxes

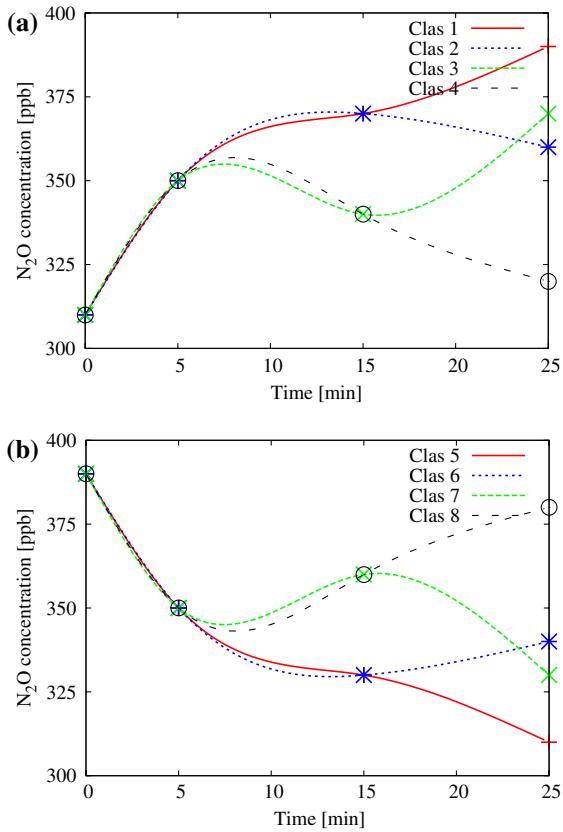

Fig. 2 Schematic representation of the eight concentration classifications

of category 1, 2, 5 and 6 were taken into account since the others are physically not explainable.

The fluxes were set to 0 ng N m^{-2} s^{-1} when the standard deviation over the concentration pattern is smaller than 10 ppb for N_2O. The gas flux is dependent on the concentration gradient following Fick's first law (Davidson et al. 2002). In the case of an emission, the concentration within the chamber increases, the concentration gradient decreases and in consequence the rise in concentration decreases. When a closed chamber measurement is performed the flux is estimated using the concentration gradient in the chamber headspace shortly after the chamber is put on the soil. The flux (F) is calculated by

$$F = h\frac{\mathrm{dC}}{\mathrm{d}t}\bigg|_{t=0} \tag{1}$$

in which h is the height of the chamber in m, C is the concentration in ppb and t is the time in s. The slope $\mathrm{d}C/\mathrm{d}t$ is the slope of the gas concentration curve which can be estimated using different methods. Often a linear regression is used to determine the flux. In general, the method of the least squares is performed to estimate the concentration gradient (Chatfield 1997). This strategy is based on fitting a straight line through the data which is represented by

$$C = a_0 + a_1 t \tag{2}$$

where a_0 indicates the y-axis interception point and a_1 indicates the slope of the curve. Estimates of a_0 and a_1 are made in a way that the line gives a good fit to the data with which the sum of squares of the difference in the observed C and the estimated $\hat{C}$ is minimized. The sum of the squared deviations is given by

$$S = \sum_{\mathrm{i}=1}^{\mathrm{n}} e_{\mathrm{i}}^2 = \sum_{\mathrm{i}=1}^{\mathrm{n}} [C_{\mathrm{i}} - (a_0 + a_1 t_{\mathrm{i}})]^2. \tag{3}$$

The corresponding estimates of a_0 and a_1 are defined by

$$\begin{aligned} \hat{a}_0 &= \bar{C} - \hat{a}_1 \bar{t} \\ \hat{a}_1 &= \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} (t_{\mathrm{i}} - \bar{t})(C_{\mathrm{i}} - \bar{C})}{\sum_{\mathrm{i}=1}^{\mathrm{n}} (t_{\mathrm{i}} - \bar{t})^2}. \end{aligned} \tag{4}$$

The goodness-of-fit is indicated by the coefficient of determination (R^2) which is described by

$$R^2 = \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} (\hat{C}_{\mathrm{i}} - \bar{C})^2}{\sum_{\mathrm{i}=1}^{\mathrm{n}} (C_{\mathrm{i}} - \bar{C})^2}. \tag{5}$$

Linear regression is mainly used because this method is very easy to apply.

However, in case of a well-mixed air within the chamber space, the concentration behaviour as function of the time is described by (de Mello and Hines 1994)

$$C(t) = C_{\max} - (C_{\max} - C_{\mathrm{air}}) \exp^{(-\mathrm{k}t)} \tag{6}$$

where $C_{\max}$ is the concentration maximum reached when the gas concentration within the chamber has become equal to the concentration of the soil atmosphere in ppb, C_{air} is the air concentration at time = 0 s in ppb and k is a rate constant. The values of $C_{\max}$, C_{air} and k are estimated iteratively using the observed concentration versus time data. The slope of the curve at time = 0 s is given by

$$\left.\frac{dC}{dt}\right|_{t=0} = k(C_{max} - C_{air}). \quad (7)$$

A third method is the intercept method. This method is an easier tool to determine the flux values than the exponential method. The slope at time = 0 s is now determined using an additional array with estimated slope values $\hat{\gamma}_i$. This array is calculated by

$$\hat{\gamma}_i = \frac{C_i - C_{i-1}}{t_i - t_{i-1}}, \quad i = 1,2,\ldots,N-1 \quad (8)$$

The linear regression of the estimated slope values $\hat{\gamma}_i$ versus time t_i gives an estimated $\hat{a}_0$value which is equal to the slope at time = 0 s.

Besides, the goodness-of-fit R^2 a goodness-of-fit χ^2 was used to compare different calculation methods. The goodness-of-fit χ^2 between modelled and measured concentrations was determined by

$$\chi^2 = \sum_{i=1}^{N} \left(C_i - \hat{C}_i\right)^2 \quad (9)$$

where C_i and $\hat{C}_i$ denote the measured and modelled concentration in ppb, respectively. This definition of χ^2 is relative. When the same data are fitted to the different models, the fit that yields a significantly smaller χ^2 indicates the better model (Livingston et al. 2006).

Results

A fast chamber measurement is used to show an example of concentration behavior within a chamber headspace. N_2O concentrations were measured during 10 min at a sampling frequency of 3.5 Hz with a QCL spectrometer at Oukoop in the Netherlands. The linear and exponential regression methods were applied on this whole concentration pattern (see Fig. 3). The estimated slope values at time = 0 s are 0.14 and 0.32 ppb s^{-1} for the linear and exponential regression method, respectively. In consequence, the N_2O flux estimate by linear regression is only 44% of the flux estimate by exponential regression. This value is close to the underestimation value stated by Kutzbach et al. (2007) for CO_2 chamber measurements.

A first validation was done on the effect of measurement time and sampling frequency on the estimated flux values based on both methods. The best slope estimate at time = 0 s is 0.32 ppb s^{-1}

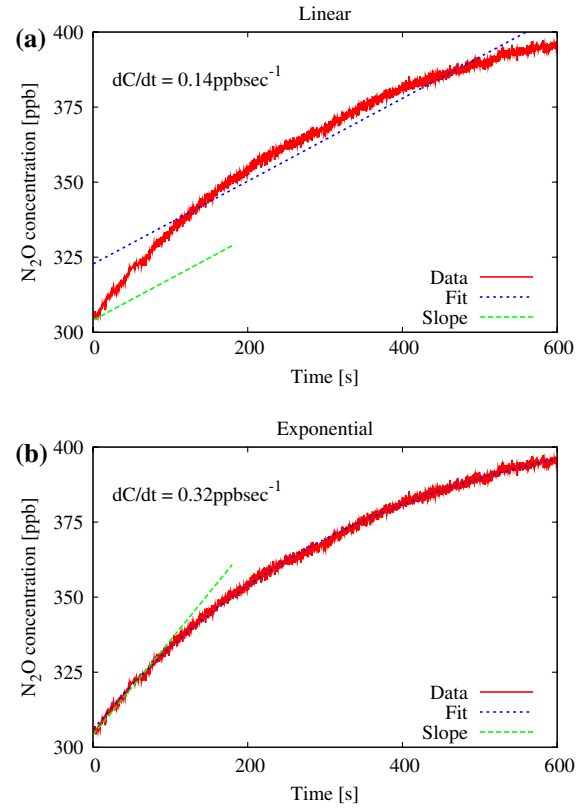

Fig. 3 Slope determination using 10 min of 3.5 Hz data with linear method (**a**) and exponential method (**b**)

which is obtained with the exponential method. Both for 3.5 Hz and six samples per minute the flux estimate of the linear and the exponential fit agree within 15% when using only the first minute of data (see Fig. 4). However already at a sampling time of 3 minutes, the linear regression method underestimates the flux by 20% and this underestimation increases drastically with time. So in this example, the linearity assumption is not valid even for short measurement times. This is also noted among others by Kutzbach et al. (2007). This non-linearity causes a systematic underestimation in the flux estimates.

Some researchers believe that this kind of concentration behavior can only be caused by leakage of the chamber. However, Livingston et al. (2005, 2006), for example, have stated that this behavior can also be caused by the gas exchange processes. An example of non-linear behavior of the gas accumulation in the chamber headspace is given in Fig. 5. The N_2O gas exchange shows a non-linear behavior while the linear increase of the C_2H_6 tracer indicates

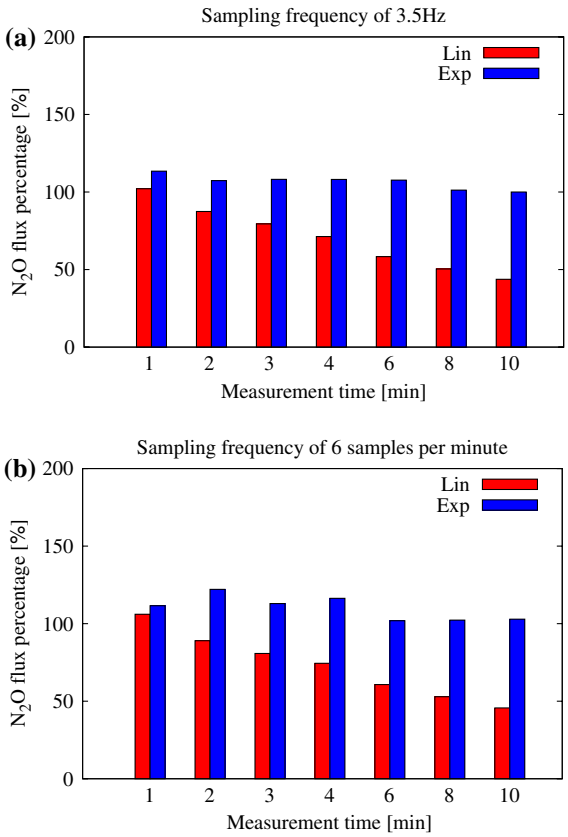

Fig. 4 Analyses of the amount of N_2O flux under- or overestimation for linear and exponential regression method for different measurement times and sampling frequencies of 3.5 Hz (**a**) and six samples per min (**b**). Assuming that the exponential method gives the correct flux based on the concentration pattern over 10 min of 3.5 Hz data

that the box is not significantly leaking. The C_2H_6 increase is close to the expected value related to the input flow of 1.6 ml min^{-1}. The conclusion is that the N_2O gas exchange is not constant over the measurement period and a linear regression method underestimates the flux.

The N_2O flux was estimated using the linear regression method (see Eq. 4) and the exponential method (see Eq. 7). The flux estimates are 85 and 150 ng N m^{-2} s^{-1} for the linear and the exponential method, respectively. Thus, the linear flux estimate is only 66% of the exponential estimate. The exponential method has the most accurate estimator based on an analysis using Eq. 9.

To further investigate the hypothesis that the linear regression method can drastically underestimate the flux over measurement periods longer than 2 min, fluxes were determined by both calculation methods over four episodes with N_2O automatic chamber measurements. Each episode covered a month of data starting 3 days before a fertilizing application. The measurement episodes started at 10 September 2005, 5 February 2006, 9 April 2006 and 14 May 2006. The N-application levels were 33, 128, 60 and 99 kg N ha^{-1}, respectively. The fertilizer application was performed within the surface area of the automatic chamber and on the surface 2 m^2 around the chamber. The four datasets have 383, 695, 756 and 603 fluxes per episode from which 99, 97, 91 and 98% had classification 1, 2, 5 or 6 (see Fig. 2). In order to compare the two regression methods, a

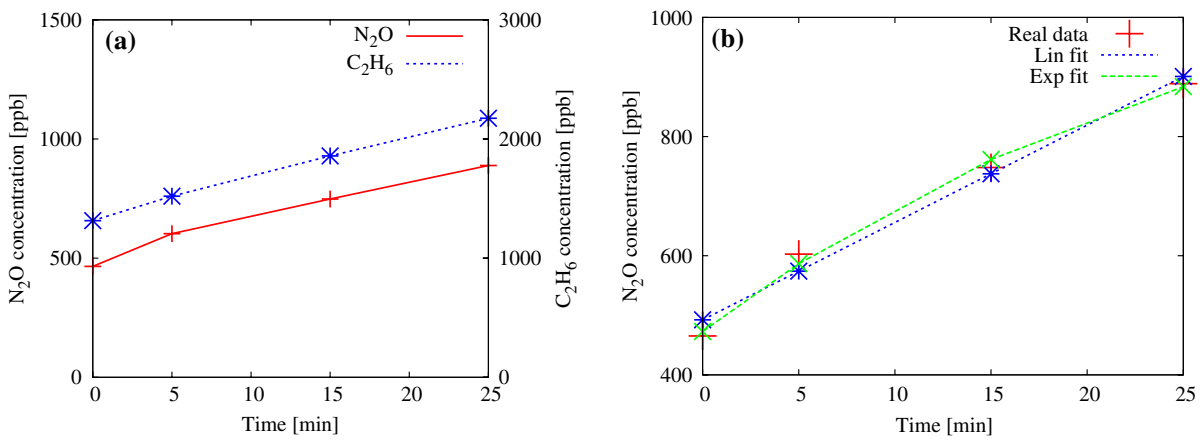

Fig. 5 Gas accumulation in the automatic chamber at Cabauw in the Netherlands for 24 May 2006 at 1600 hours (**a**). An overview of the real measured N_2O data, and the linear and exponential fitted data corresponding to this flux (**b**)

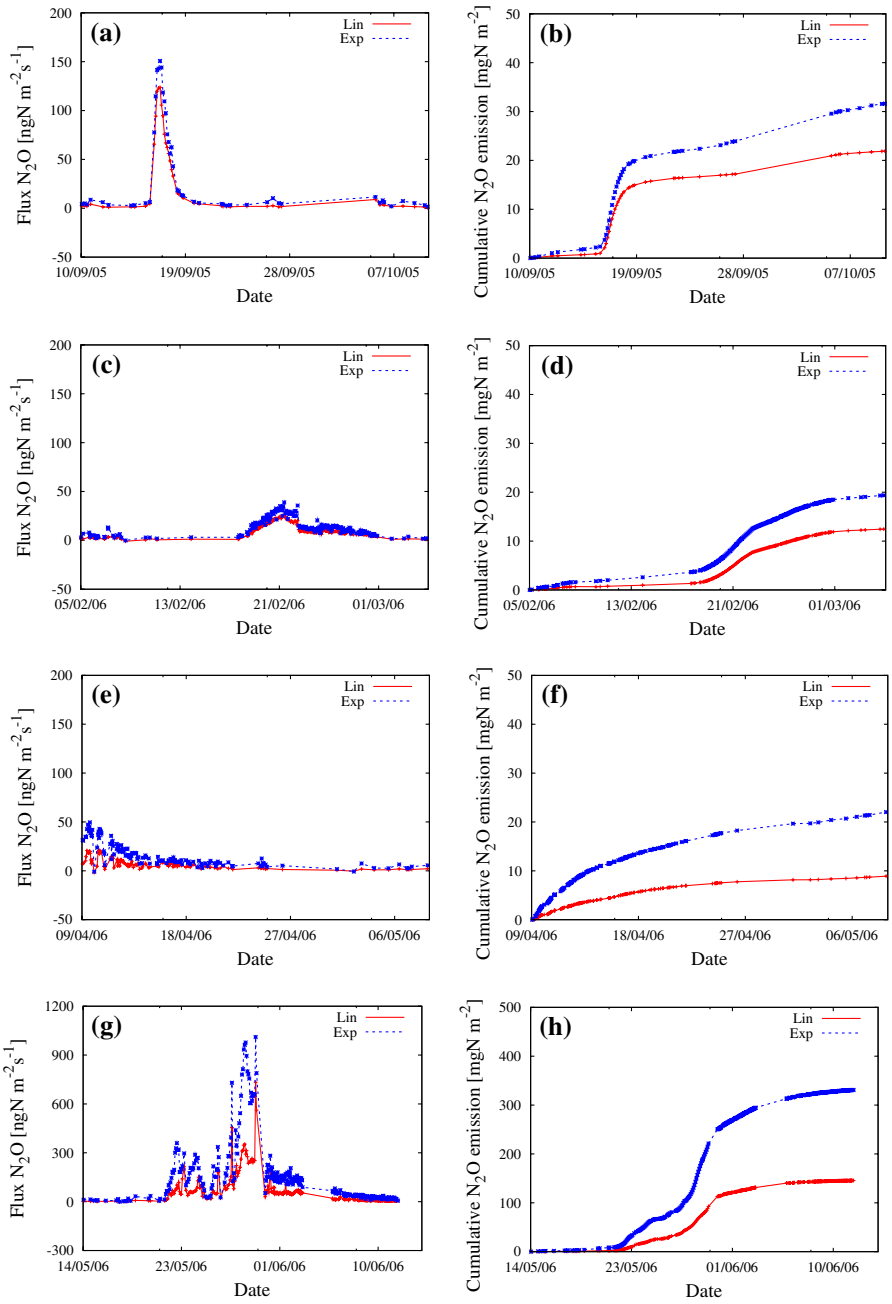

Fig. 6 Fluxes (**a**, **c**, **e**, **g**) and cumulative (**b**, **d**, **f**, **h**) N_2O emissions from 3 days before until 1 month after fertilizing of the September 2005, February 2006, April 2006 and March 2006 fertilizing events

subset of data was used that satisfied respective quality checks for both methods. For the linear regression, R^2 should be larger than 0.75. For the iterative exponential method, the relative standard deviation of the estimates of C_{max}, C_{air} and k should be smaller than 150%. Finally, 13, 25, 18 and 45% of the fluxes were used for validating the difference in the four episodes. The data reduction is significant mainly due to the exponential method; however, mainly small fluxes were rejected. The effect of this selection on the cumulative flux in each episode, however, is almost negligible. This will be shown later.

The N_2O fluxes and the cumulative emissions are shown for all four fertilizing events in Fig. 6. The cumulative emissions based on the linear regression differ a lot with the cumulative emissions based on the exponential method. The cumulative emissions

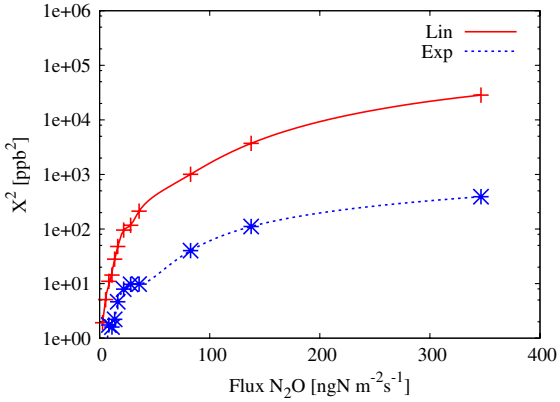

Fig. 7 Goodness-of-fit (χ^2) of linear and exponential regression method to N_2O automatic chamber measurements as a function of the N_2O flux. Data points represent the average goodness-of-fit and average N_2O flux over a bin including hundred N_2O fluxes

obtained with the linear fit method are only 69, 63, 41 and 44% of the cumulative emissions estimated with the exponential fit method of the September 2005, February 2006, April 2006 and May 2006 fertilizing events, respectively. The goodness-of-fit is evaluated for each flux using Eq. 9. The exponential regression method gives more accurate responses than the linear regression method (see Fig. 7).

Assuming that the exponential method gives the correct results, the maximum flux values in the subsequent episodes are 151, 39, 50 and 1,011 ng N m^{-2} s^{-1} for September, February, April and May, respectively. Clear flux peaks occurred after the fertilizing events in September, February and May. The fluxes started to peak on 16 September, 18 February, 21 May and 27 May. There was no peak after the fertilization application in April and there were two peaks after the fertilization application in May. All four peaks occurred within 2 days after heavy precipitation (>10 mm day^{-1}). The total amounts of emitted N_2O-N within each episode are 1.0, 0.2, 0.4 and 3.4% of the applied N. These values are comparable with other studies (e.g., Eichner 1990; Clayton et al. 1994; Chadwick et al. 2000; Flechard et al. 2007). The difference in the amount of emitted N_2O-N are known to be related with temperature and precipitation as indicated by Christensen (1983) and Bothe et al. (2007), but this evaluation is not the focus of this study. The temperature and precipitation rates have been made available by the KNMI in the Netherlands. In Table 2, a summary is given of the applied N, percentage emitted N_2O-N, average air temperature and precipitation rates.

It is clear that, in this case, the use of an exponential method is required for estimating the N_2O fluxes, because the goodness-of-fit is much better for the exponential method than the linear regression method. The exponential method has been recommended in several studies, e.g., de Mello and Hines (1994). Nevertheless, almost no N_2O chamber measurement studies are published based on this calculation method. It is obvious that the exponential fit method requires three and preferable more measurements per chamber measurement cycle. They are needed to obtain information on the curvature of the slope.

Measurement sets that only have a start and end concentration cannot use this method. Another reason not to use the exponential method is the higher complexity of this method in comparison with the linear regression method. Therefore, the more easily

Table 2 Summary of applied N and N_2O emissions of four fertilizing events at Cabauw in the Netherlands

Measurement period	Measurement method	Applied N (kgN ha^{-1})	Cumulative emissions N_2O-N (kgN ha^{-1})	Percentage emitted N_2O-N (%)	T (°C)	R (mm)
10/09/05–10/10/05	Linear	33	22×10^{-2}	0.7	14	114
	Exponential		32×10^{-2}	1.0		
05/02/06–05/03/06	Linear	128	12×10^{-2}	0.1	3	58
	Exponential		19×10^{-2}	0.2		
09/04/06–09/05/06	Linear	60	9×10^{-2}	0.1	11	15
	Exponential		22×10^{-2}	0.4		
14/05/06−14/06/06	Linear	99	146×10^{-2}	1.5	13	84
	Exponential		331×10^{-2}	3.4		

applicable intercept method is evaluated in this study. This method also requires at least three measurement points per chamber cycle.

The exponential regression method estimates and the intercept method estimates were compared for the four monthly episodes with automatic chamber data. In Fig. 8, it is shown that the estimates based on the intercept method are close to those obtained with the exponential method. The total amounts of emitted N_2O-N within each episode calculated with the intercept method are 1.0, 0.2, 0.3 and 3.1%. All these levels are close to the results obtained with the exponential method. The influence of rejecting fluxes is studied using the intercept method. The cumulative emissions are calculated over each episode without rejecting any flux. This means that also fluxes with a classification 3, 4, 7 and 8 are taken into account. In this case, the percentage emitted N_2O-N is 0.8, 0.1, 0.3 and 3.1%. These levels are close to the emitted N_2O-N values based on the accepted fluxes only. The

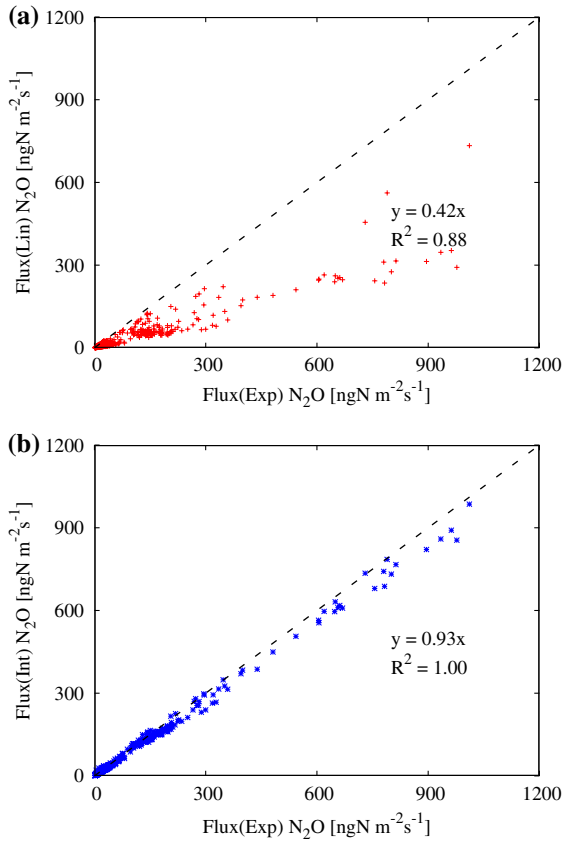

Fig. 8 Comparison of the fluxes calculated by the exponential method with the linear method (**a**) or intercept method (**b**)

conclusion is that the cumulative emissions are well estimated for all four fertilizing episodes.

The intercept method is a good and easy alternative both in case of an exponential concentration behavior and in case of a linear concentration behavior under the chamber headspace. The method is only based on the slope of the curve as function of time with which the slope at time 0 s is derived. If the concentration profile is linear, the intercept method and linear regression method will give both exact the same flux estimate.

It is recommended to validate the different methods for each dataset using a goodness-of-fit analysis based on Eq. 9. In these experiments, the additional tracer was used as well to determine the most convenient calculation method. C_2H_6 was added to the flow at a rate of 1.6 ml min^{-1} during the May fertilizing event. The C_2H_6 fluxes over this period were calculated with the linear and intercept method. The cumulative emissions obtained with the linear method underestimate the C_2H_6 input by 60%. However, using the intercept method only 10% difference is obtained between the expected and estimated flux (see Fig. 9). Assuming an equal systematic error both for the C_2H_6 tracer and for N_2O a corrected N_2O flux is calculated by

$$F_i^{cor}(N_2O) = Cor_i F_i^{Lin}(N_2O) \tag{10}$$

where i denotes the flux number, $F_i^{lin}(N_2O)$ the linear derived flux value and Cor_i the correction factor which is described by

$$Cor_i = \frac{F_i^{Real}(C_2H_6)}{F_i^{Lin}(C_2H_6)} \tag{11}$$

In which $F_i^{real}(C_2H_6)$ and $F_i^{lin}(C_2H_6)$ are the real added flux and the linear regression derived flux of the C_2H_6 tracer. The cumulative corrected N_2O emission is close to the cumulative intercept calculated emission (see Fig. 9).

The C_2H_6 tracer is an additional tool to validate the expected systematic error for each calculation method.

The systematic error due to the calculation method is often ignored since the uncertainties due to spatial and temporal variation in N_2O exchanges are assumed to be much larger. However, in a study by Flechard et al. (2007), the overall uncertainty in annual flux estimates derived from chamber measurements is estimated to be 50% due to the temporal

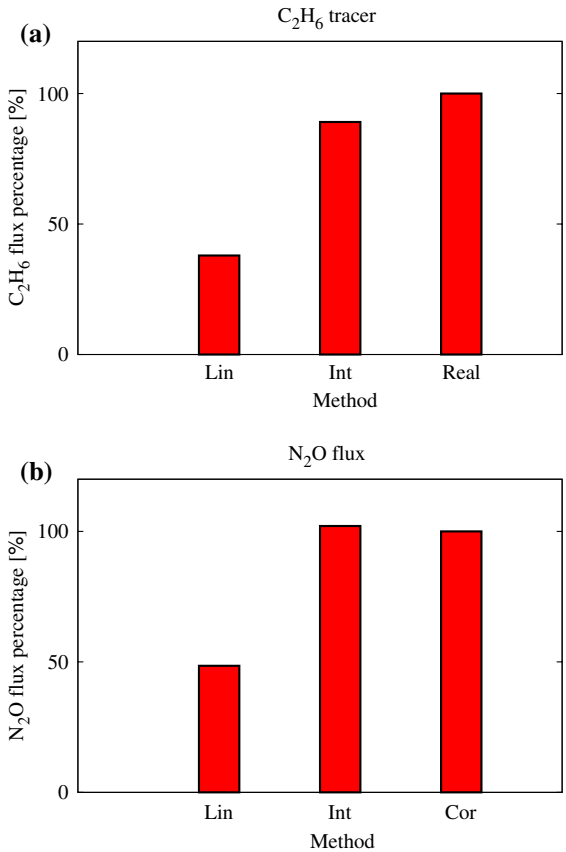

Fig. 9 Comparison of real cumulative C_2H_6 added flow and calculated C_2H_6 added flow with the linear and intercept method (**a**). Comparison of cumulative N_2O emission with the linear, intercept and C_2H_6 tracer corrected method (**b**)

and spatial variability in the fluxes. For our experiment, this uncertainty is of the same order as the estimated systematic error in the calculation method. Therefore, the systematic error due to the calculation method can not be ignored. In addition, an example is given of the uncertainty due to temporal variation for our case study.

Example: temporal variation

Often chamber measurements are performed with manual mobile systems on a weekly or bi weekly basis. This is a source of another important uncertainty in net annual exchange calculated from chamber measurement data. It is not the aim of this paper to elaborate on temporal sampling schemes, but it is useful to compare this uncertainty with the systematic error due to the calculation methods. The continuous measurements were sub sampled to simulate a weekly measurement scheme (see Fig. 10). For the first measurement point, data was used obtained three days before fertilizing. This flux was assumed to be representative for the episode until the fertilizing day. The other measurements were selected in weekly intervals from the continuous dataset. Triangular integration (the surface under the line connecting measurement points) was used to obtain the cumulative emissions. The cumulative emissions calculated with the continuous and weekly measurements differ at most by 50% which is of the same order as the uncertainty by the calculation method.

Conclusions

The importance of reducing the systematic error due to non-linearity in N_2O flux measurements by static chambers was validated with 4 months of data measured by a near-continuous automatic chamber. The data cover four fertilizing events in episodes of 1 month in September 2005, February 2006, April 2006 and May 2006, respectively. The linear regression, exponential regression and intercept method were compared. The exponential regression gives more accurate responses than the linear regression based on a goodness-of-fit analysis. The exponential method accounts for the effect of equilibrium of the concentration in the chamber with the soil concentrations. The cumulative emissions of the intercept method are close to the cumulative emissions of the exponential method. The cumulative estimates with the linear regression method are 60% below of the cumulative estimates with the exponential regression method. The difference in performance of the calculation method is also demonstrated with a C_2H_6 tracer. The reasons for the non-linearity can be different, like damping of the diffusion controlled part of the flux, pressure effects and leaking effects. The degree of underestimation reported here is therefore a specific result for our combination of terrain and measurement set-up and might be smaller at other sites. The uncertainty in the net exchange due to the spatial variability as well as the uncertainty that would occur with weekly sampling in stead of continuous sampling can be of the same order as the systematic error due to the calculation method.

The total emitted N_2O-N within the four fertilizing periods is 1.0, 0.2, 0.4 and 3.4%. The differences are

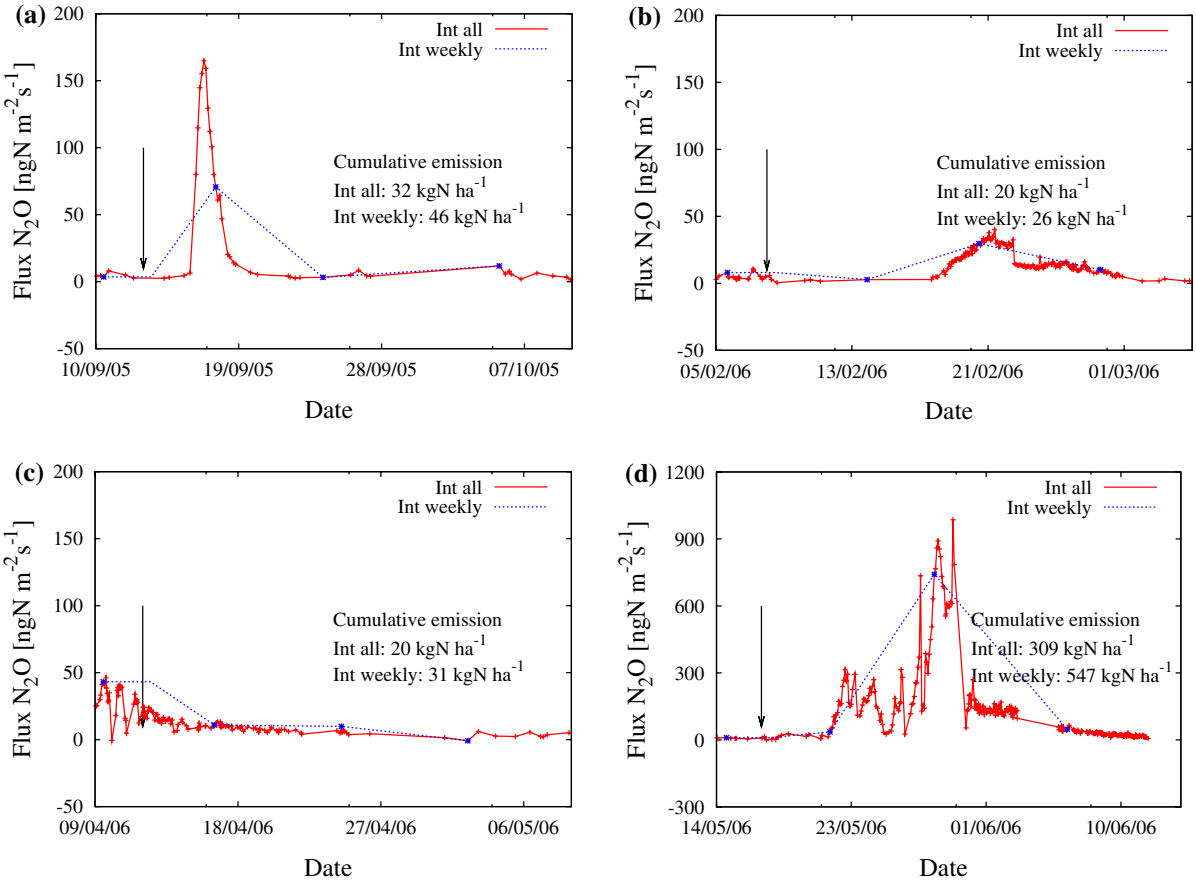

Fig. 10 Comparison of cumulative N_2O emission measured continuously and weekly at Cabauw in the Netherlands in September 2005 (**a**), February 2006 (**b**), April 2006 (**c**) and May 2006 (**d**). The *black arrow* indicates the moment of fertilizing

probably partly caused by temperature and precipitation.

Clear peaks in the flux occurred in the September, February and May fertilizer events. The fluxes peaked within 2 days after heavy precipitation (>10 mm day^{-1}).

Concluding, closed-chamber data should always be tested for non-linearity and an appropriate method should be used to calculate the flux. The systematic error due to non-linearity can not be ignored in comparison to the uncertainty due to spatial and temporal variation. Only a filter on $R^2 > 0.75$ is not sufficient to cancel the effect of non-linearity. Studies based on two measurements one at the beginning and one at the end of the chamber closure time, should also check the systematic error due to non-linearity based on an additional small set of concentration profiles. If the measurements show a linear or exponential concentration profile, the intercept method can be applied. The performance of each method can be validated using a tracer and a goodness-of-fit analysis.

Acknowledgements This research was part of the CarboEurope project and the Dutch BSIK program. We thank our colleagues P. Fonteijn, T. Schrijver and H. van 't Veen for their assistance during setting-up these experiments. We are also very grateful to E. de Beus of Technical University of Delft and G. Pieterse of University of Utrecht for their assistance in data analyses. D. Hendriks of University of Amsterdam and A. Schrier-Uijl of University of Wageningen are acknowledged for the discussions. Finally, we owe a special debt of gratitude to the KNMI and the farmer T. van Eyk for using their sites.

References

Anthony WH, Hutchinson GL, Livingston GP (1995) Chamber measurement of soil-atmosphere gas exchange: linear vs. diffusion-based flux models. Soil Sci Soc Am J 59: 1308–1310

Beljaars ACM, Bosveld FC (1996) Cabauw data for the validation of land surface parameterization schemes. J Clim 10:1172–1193

Bothe H, Ferguson SJ, Newton WE (2007) Biology of the nitrogen cycle. Elsevier, The Netherlands

Chadwick DR, Pain BF, Brookman SKE (2000) Nitrous oxide and methane emissions following application of animal manures to grassland. J Environ Qual 29:277–287

Chatfield C (1997) Statistics for technology: a course in applied statistics. Chapman & Hall, UK

Christensen S (1983) Nitrous oxide emission from a soil under permanent grass: seasonal and diurnal fluctuations as influenced by manuring and fertilization. Soil Biol Biochem 15:531–536

Clayton H, Arah JRM, Smith KA (1994) Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. J Geophys Res 99:16599–16607

Conen F, Smith KA (2000) An explanation of linear increase in gas concentration under closed chamber used to measure gas exchange between soil and the atmosphere. Eur J Soil Sci 51:111–117

Crutzen PJ (1981) Atmospheric chemical processes of the oxides of nitrogen, including nitrous oxide. Wiley, New York

Davidson EA, Savage K, Verschot LV et al (2002) Minimizing artifacts and biases in chamber-bases measurements of soil respiration. Agric For Meteorol 113:21–37

De Mello WZ, Hines ME (1994) Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in Spagnum peatlands: implications for the magnitude and direction of the flux. J Geophys Res 99:14601–14607

Eichner MJ (1990) Nitrous oxide emissions from fertilized soils: summary of available data. J Environ Qual 19:272–280

Flechard CR, Ambus P, Skiba U et al (2007) Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe. Agric Ecosyst Environ 121:135–152

Gao F, Yates SR (1998) Laboratory study of closed and dynamic flux chambers: experimental results and implications for field application. J Geophys Res 103: 26115–26125

Hansen S, Maehlum JE, Bakken LR (1993) N_2O and CH_4 fluxes in soil influenced by fertilization and tractor traffic. Soil Biol Biochem 25:621–630

Healy RW, Striegl RG, Russell TF et al (1996) Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange: identification of physical processes. Soil Sci Soc Am J 60:740–747

Hendriks DMD, Huissteden J, Dolman AJ (2007) The full greenhouse gas balance of an abandoned peat meadow. Biogeosciences 4:411–424

Hutchinson GL, Mosier AR (1981) Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Sci Soc Am J 45:311–316

IPCC Climate change 2001 (2001) The scientific basis. Cambridge University Press, Cambridge

IPCC Climate change 1995 (2006) Scientific and technical analyses of impacts, adaptations and mitigation. Contribution of working group II to the second assessment report of the intergovernmental panel on climatic change. Cambridge University Press, London

Jager CJ, Nakken TC, Palland CL (1976) Bodemkundig onderzoek van twee graslandpercelen nabij Cabauw (in Dutch). NV Heidemaatschappij Beheer, The Netherlands

Kroon PS, Hensen A, Jonker HJJ et al (2007) Suitability of quantum cascade laser spectroscopy for CH_4 and N_2O eddy covariance flux measurements. Biogeosciences 4:715–728

Kutzbach L, Schneider J, Sachs T et al (2007) CO_2 flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression. Biogeosciences 4:1005–1025

Laville P, Jambert C, Cellier P et al (1999) Nitrous oxide fluxes from a fertilized maize crop using micrometeorological and chamber methods. Agric For Meteorol 96:19–38

Livingston GP, Hutchinson GL, Spartalian K (2005) Diffusion theory improves chamber-based measurement trace gas emission. Geophys Res Lett 32:L24817, doi:10.1029/2005GL024744

Livingston GP, Hutchinson GL, Spartalian K (2006) Trace gas emission in chambers: a non-steady state diffusion model. Soil Sci Soc Am J 70:1459–1469

Pederson AR, Petersen SO, Vinther FP (2001) Stochastic diffusion model for estimating trace gas emissions with static chambers. Soil Sci Soc Am J 65:49–58

Piphlatie M, Rinne J, Ambus P et al (2005) Nitrous oxide emissions from a beech forest Floor measured by eddy covariance and soil enclosure techniques. Biogeosciences 2:377–387

Ruser R, Flessa H, Schilling R et al (1998) Soil compaction and fertilization effects on nitrous oxide and methane fluxes in potato fields. Soil Sci Soc Am J 62:1587–1595

Veenendaal EM, Kolle O, Leffelaar P et al (2007) Land use dependent CO_2 exchange and carbon balance in two grassland sites on eutropic drained peat soils. Biogeosciences 4:1027–1040