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A case study of eddy covariance flux of N_2O measured within forest ecosystems: quality control and flux error analysis

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Abstract

Eddy covariance (EC) flux measurements of nitrous oxide obtained by using a 3-D sonic anemometer and a tunable diode laser gas analyzer for N_2O were investigated. Two datasets (Sorø, Denmark and Kalevansuo, Finland) from different measurement campaigns including sub-canopy flux measurements of energy and carbon dioxide are discussed with a focus on selected quality control aspects and flux error analysis. Although fast response trace gas analyzers based on spectroscopic techniques are increasingly used in ecosystem research, their suitability for reliable estimates of eddy covariance fluxes is still limited, and some assumptions have to be made for filtering and processing data. The N_2O concentration signal was frequently dominated by offset drifts (fringe effect), which can give an artificial extra contribution to the fluxes when the resulting concentration fluctuations are correlated with the fluctuations of the vertical wind velocity. Based on Allan variance analysis of the N_2O signal, we found that a recursive running mean filter with a time constant equal to 50 s was suitable to damp the influence of the periodic drift.

Although the net N_2O fluxes over the whole campaign periods were quite small at both sites ($\sim 5\,\mu g\,N\,m^{-2}\,h^{-1}$ for Kalevansuo and $\sim 10\,\mu g\,N\,m^{-2}\,h^{-1}$ for Sorø), the calculated sub-canopy EC fluxes were in good agreement with those estimated by automatic soil chambers. However EC N_2O flux measurements show larger random uncertainty than the sensible heat fluxes, and classification according to statistical significance of single flux values indicates that downward N_2O fluxes have larger random error.

1 Introduction

Nitrous oxide (N_2O) is a strong greenhouse gas having the greatest greenhouse warming potential over a long period (100 years), which is about three hundred times larger than the one of carbon dioxide (IPCC, 2001). Microbial activity in soil ecosystems is the major source of N_2O to the atmosphere (IPCC, 2001). Agricultural soils are the major sources of N_2O, however, due to their large areal coverage, forest soils have a substantial contribution to the total emissions of N_2O (e.g. Skiba et al., 1994; Kesik et al., 2005).

Thanks to recent development of fast response N_2O analyzers based on spectroscopic techniques (e.g. tunable diode laser (TDL) and quantum cascade laser (QCL) spectrometers), the eddy covariance method has become an approach, which is potentially suitable for measuring long-term and spatially integrated N_2O fluxes.

Such method is routinely used in many micrometeorological sites worldwide to measure CO_2 and H_2O fluxes above and below forest canopies, thanks to well established methodologies (Aubinet et al., 2000), long term stability of the fast response analysers of those trace gases and high signal-to-noise ratios of sampled concentrations. In case of N_2O it is not straightforward that these requirements for reliable estimations of EC fluxes are fulfilled. Several studies have demonstrated that the N_2O emissions are episodic in nature, showing high spatial and temporal variability, due to large variation in soil properties such as soil moisture, availability of nitrogen and easily decomposable organic matter (Ambus and Christensen, 2005; Pihlatie et al., 2005; Silver et al., 2005). Moreover the performance and stability of fast response N_2O analyzers strongly depends on the instrumental drift, which typically characterizes TDL and QCL spectrometers (Werle et al., 1993; Nelson et al., 2002). Up to now only a limited number of N_2O EC measurements have been reported in literature and they have been mainly carried out in agricultural soil ecosystems (Smith et al., 1994; Wienhold et al., 1994; Christensen et al., 1996; Laville et al., 1999; Scanlon and Kiely, 2003; Neftel et al., 2007; Kroon et al., 2007), and forest soil ecosystems (Pihlatie et al., 2005; Eugster et al., 2007).

Large uncertainty and temporal variability of EC N_2O fluxes, reported by these studies, is related either to biogeochemical soil processes and/or several systematic and random error sources of the EC measurements.

In this case study we explore the limits of eddy covariance flux measurements of N_2O using state-of-the art equipments. We present a detailed evaluation of the main error sources and uncertainties of EC N_2O fluxes measured within two different forest ecosystems, a beech forest in Sorø, Denmark, and a Scots pine forest in Kalevansuo, Finland, during two distinct measurement campaigns. Both field campaigns were carried out in the trunk space layer. Chamber flux data obtained during both campaigns are used as reference, and recommendations how to treat data for post-processing are derived from the assumption that below-canopy eddy covariance flux measurements should match the temporal pattern and magnitude of chamber flux measurements, although also chambers are prone to systematic errors.

EC system performances are investigated by using the Allan variance concept (Werle et al., 1993). We explored the effect of instrumental drift of the N_2O signal on the EC flux, and we proposed a criterion for selecting a suitable time constant of the high pass filter, which is necessary method to apply in order to remove the drift. Flux error analysis, traditionally used in the micrometeorological community for energy and CO_2 fluxes, are discussed and applied to N_2O flux measurements, in order to identify uncertainty of fluxes caused by instrumentation problems and systematic as well as random errors. Finally for validation purposes we compare the EC fluxes with those obtained by soil chamber technique.

2 Site description and measurements

The first measurement campaign was conducted from 2 May to 5 June 2003 in a 87 year old beech (*Fagus sylvatica* L.) forest near Sorø on the island of Zealand, Denmark. The forest is located in a flat terrain and extends 1 km in the east-west direction and 2 km in north-south direction. The beech trees are 25 m tall, but the forest also contains scattered stands of conifers. Mean leaf area index (LAI) for the main footprint of the forest is 5 $m^2\,m^{-2}$. The LAI is approximately constant between June and September and drops slowly during the autumn. During the campaign EC N_2O fluxes were measured in the sub-canopy layer at 3 m height from the forest floor by using a small mast. The EC system consisted of a 3-D sonic anemometer (Solent 1012, Gill) and a TDL gas analyser (TGA 100, Campbell Scientific Inc.). Soil N_2O fluxes were also obtained by using chamber technique. More details on chamber setup and data processing are given in Pihlatie et al. (2005).

The second measurement campaign was conducted during the spring 2007 (25 April to 27 June) at a Kalevansuo drained peatland forest. The site was located in southern Finland (60°39′ N, 24°22′ E), where the mean annual precipitation is 606 mm and the mean annual temperature is 4.3°C. The canopy height is about 16 m, the tree stand is uneven, gappy and unclosed, and consists mainly of Scots pine (*Pinus sylvestris* L.) with some small-sized Norway spruce (*Picea abies* L.) and downy birch (*Betula nana*) in the gaps near ditches.

The main measurements included micrometeorological eddy-covariance (EC) measurements of CO_2, H_2O and N_2O fluxes at 4 m height, and chamber based measurements of N_2O fluxes. Sub-canopy CO_2 and H_2O fluxes were measured by a Li-7500 Open-Path Infrared CO_2/H_2O Gas Analyzer (Li-Cor Inc.) and a CSAT3 Sonic Anemometer (Campbell Scientific Inc.). Eddy covariance measurements of N_2O fluxes were conducted at the same mast using the same CSAT3 anemometer and a tunable diode laser spectrometer (TGA-100A, Campbell Scientific Inc.).

Soil fluxes of N_2O were also measured by enclosure method using automatic and manual chambers. The nine automatic chambers sampled continously by gaschromatography were located approximately 100 m southwest from the sub-canopy EC mast. More details on chamber setup and data processing are given in Pihlatie et al., 2009.

The TDL system used in both sites consists of a temperature and current controlled single mode diode laser, tuned to an infrared N_2O absorption band and mounted in a liquid nitrogen Dewar. Concentration measurement was achieved by passing the infra red laser beam through the sample and reference cells. The reference gas (2000 ppm N_2O from a steel cylinder – Messer Griesheim, Germany for Kalevansuo and Oy Aga Ab, Linde Gas for Sorø) was drawn through the reference cell under same temperature and pressure conditions as the sample air in the sample cell (see Table 1 for temperature and pressure values). The sample air was drawn to the TDL analyzer with a Busch rotary-vane pump (RB0021-L) via a diffusive dryer (PD1000, Perma pure Inc.) to remove excess water vapour that could infer the analysis. Sample air leaving the dryer was directed to the TDL analyzer via 10 m long Teflon tubing (inner diameter 4 mm) for Sorø and 4 m for Kalevansuo (inner diameter 4.25 mm). The total volume of the inlet system was approximately 0.24 l and that of the sample cell 0.48 l. The sample flow rate was 14 l min^{-1} for Sorø and 15 l min^{-1} for Kalevansuo experiment. The residence time in the sample cell was approximately 0.1 s, which is sufficient to provide the necessary exchange time for flux measurements.

During the measurement period, pressure inside the sample cells was kept constant at approximately 70 mbar for Sorø and 50 mbar for Kalevansuo and at both sites the measurements were conducted at 10 Hz frequency. The TDL was calibrated once during the measurement period using zero and span (290.3 ppb N_2O) calibration gases. The setup details and operational parameters according to the data sheet of the two EC-TDL systems are summarized in Table 1.

3 Methods

3.1 EC measurements: data processing and corrections

The eddy covariance fluxes were calculated as 30 min co-variances between the scalars and vertical wind velocity according to commonly accepted procedures (Aubinet et al., 2000). Prior to calculate the turbulent fluxes a 1-D rotation (mean lateral wind equal to zero) of sonic anemometer wind components and filtering to eliminate spikes were performed according to standard methods (Vickers and Mahrt, 1997).

All signals were detrended for removing the average values and trends. As a first step a linear detrending (LDT) procedure was used. However the N_2O signal measured by the TDL gas analyzer was frequently dominated by low frequencies noise, which is mainly due to optical interference fringes (Campbell TDL Reference Manual;

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀I I▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Hernandez, 1986; Werle et al., 2004; Brodeur et al., 2008). Offset drifts can be observed, which are due to small variations of the TDL optical properties caused by small changes of the instrument temperature (Smith et al., 1994), which in turn has strong effect on the system performance and the flux detection limit. In order to suppress the instrumental drift effect and to reduce the flux random variability, the N_2O flux was also calculated after applying an autoregressive running mean filter (RMF, McMillen, 1988) to the sampled signals. Although this approach was adopted previously for post-processing drifting concentration signals (Billesbach et al., 1998; Kormann et al., 2001; Kroon et al., 2007), the choice of the high pass time constant is not straightforward and objective choosing methods are rare in literature. Methods based on signal auto-correlation coefficient and spectral analysis likely fail to give a reliable estimation of the timescale at which the drift effect becomes important, because of non-stationarity nature of the low frequency signal noise. In this study we used the concept of the Allan variance, as proposed by Werle et al., 1993. This technique is a valuable tool to assess the precision and stability of TDL spectrometers and has been used to get an estimate for the time constant for the running mean filter as described in Sect. 4.1.

The lag time between the N_2O signal and vertical wind speed was determined by maximizing the corresponding cross-covariance function, using a procedure similar to Pihlatie et al. (2005). The measured N_2O lag time was about 1 s for Kalevansuo and 2 s for Sorø. For further corrections and validation of the fluxes co-spectra of sensible heat, CO_2 (only for Kalevansuo) and N_2O were calculated using fast Fourier transform (FFT) on linearly de-trended segments of 2^{15} data points (about one hour periods). In order to reduce the random uncertainty, the single co-spectra were ensemble averaged according to atmospheric stability.

In order to quantify the high frequency flux loss, a below canopy co-spectral model was empirically derived by fitting the sensible heat co-spectra $Co_{w\theta}$, to this simple functional form:

$$\frac{fCo_{w\theta}(f)}{\overline{w\theta}} = \frac{n}{n_m}\left[1 + m\left(\frac{n}{n_m}\right)^{2\mu}\right]^{-\frac{1}{2\mu}\left(\frac{m+1}{m}\right)} \qquad (1)$$

where f is the natural frequency in Hz, $n{=}fz/U$ is the normalized frequency, z the EC measurement level, U the mean wind velocity, m is the inertial slope parameter (which should be equal to 3/4 in order to get the −4/3 inertial sub-range power law of the co-spectrum $f\mathrm{Co}_{w\theta}(f)$), μ is the broadness parameter and n_m is the normalized frequency at which the logarithmic co-spectrum $f\mathrm{Co}_{w\theta}(f)$ attains its maximum value (Lee et al., 2004). The measured sensible heat co-spectra were fitted to the Eq. (1) by non-linear regression obtaining the parameters m, μ and $n_{m.}$ The results are discussed in the Sect. 4.4.

All fluxes were corrected for different low-pass filtering effects (Moncrieff et al., 1997) by using the empirical co-spectral model and theoretical transfer functions by Moncrieff et al. (1997) which assumes co-spectral similarity between fluxes of CO_2, N_2O and sensible heat. The correction for density fluctuations (Webb et al., 1980) was not necessary for N_2O flux measurements because moisture has been removed by using a high flow sample dryer in the system (PD1000 Nafion® dryer, Campbell Scientific, Inc., Logan, UT, USA).

3.2 Random error of flux estimates

The time-averaged co-variance $\overline{w'c'}$ is a random variable estimated over a finite realisation and its average departure from the ensemble average $<w'c'>$ is presented by the random error δF, which is a measure of one standard deviation of the random uncertainty of turbulent flux observed over an averaging period T (Lumley and Panofsky, 1964, Lenschow et al.,1994). The random error δF associated with $\overline{w'c'}$ is generally due to stochastic nature of turbulence and instrumental noise.

The random error δF of turbulent flux observed over an averaging period T was evaluated according to Vickers and Mahrt (1997)

$$\delta F = \sigma_F N^{-1/2} \tag{2}$$

where the period T is divided into N sub-records and $\sigma_F=(<F_i^2>-<F_i>^2)^{1/2}$ is the standard deviation of the sub-record average fluxes F_i ($i=1, \ldots N$), where $<>$ denotes averaging over N sub-record values.

4 Results

4.1 TDL system stability and performance

The ability of performing EC flux measurements by using the EC-TDL system depends on the accuracy and stationarity of the N_2O signal measured by the TDL spectrometer. Moreover the system needs to operate continuously under field conditions. In order to investigate the short term stability of the N_2O gas analyzer, the system was evaluated in the laboratory by sampling a constant source of N_2O from closed laboratory room. The flow system was the same than what was used in the field, resulting in similar sample flow and cell pressure. An Allan variance analysis was performed to the N_2O concentration measurements and the 10Hz noise level (std) of TDL was estimated to be 1.5 ppbv, which is in line with the system specifications from the manufacturer.

The system performance depends on the drift of the instrument, which is mainly due to optical interference fringes (Hernandez, 1986). The movement of the fringes (and thus the change in the N_2O offset) is influenced by the instrument temperature (Smith et al., 1994), and it can contaminate the flux in the case that (1) these offset drift changes are faster compared to the eddy correlation averaging time and (2) the resulting concentration fluctuations are correlated with the vertical wind velocity fluctuations. This is particularly true under field conditions, where the temperature changes cannot be fully controlled as compared to a laboratory environment. During both measurement campaigns, although both TDL systems were collocated inside the TDL box and the insulated enclosure cover, recommended by the manufacturer, was used in order to dampen diurnal temperature variations, we frequently observed such a drift in the N_2O concentration signal, which cannot be related to non-steady-state conditions of turbulent motions, since other scalars were not affected. An example is given in Fig. 1, where one hour of N_2O and temperature measurements is displayed. The N_2O concentration signal has a wave-like shape, which is not properly removed by using a LDT operation. For this case we found that a recursive high pass filter with a time constant equal to 50 s suppresses the influence of low frequency drift to the N_2O signal. By using larger time constants (100 and 200 s), the running mean tends to lag with respect to the actual trend. Figure 2 shows the corresponding Allan variance and FFT spectra of N_2O and T signals. In the lower part of Fig. 2 we can see that there is a correspondence between the slope α of the FFT spectrum and the slope β of the Allan variance, e.g. $\alpha=(-\beta-1)$. For example, $\alpha=0$ corresponds with $\beta=-1$ for white noise, and $\alpha=-3$ corresponds with $\beta=2$ for a linear drift (Werle et al., 1993).

The N_2O Allan variance (Fig. 2a) indicates that the signal is dominated by white noise up to about 5 s and it starts to drift after 50 s. Both regimes are clearly observable in the time domain (Allan variance) as well as in the frequency domain (spectrum), and they are identified by the corresponding slopes α and β. For comparison the temperature does not show any such drift at large timescales (low frequencies), but mainly consists of two domains: an inertial sub-range and a domain showing a slope $\beta=0$ ($\alpha=-1$), likely related to inactive turbulent eddies (Katul et al., 1998), penetrating down into sub-canopy layer. It seems that the low frequency range of the N_2O signal (<0.02 Hz) is mainly dominated by instrumental drift, which can give an artificial extra contribution to the fluxes when the resulting concentration fluctuations are correlated with the fluctuations of the vertical wind velocity. For all analysed cases, when the N_2O signal was dominated by a fringe effect, we found that a high-pass filter time constant of 50 s was suitable to damp the influence of the periodic drift.

The same analysis was done with Sorø N_2O timeseries and similar results were found (not shown). However the fringe effect was observed less frequently during the Sorø campaign and mainly during the first half of the measurement period.

4.2 Footprint analysis

Footprint analysis for the Sorø site was already published by Pihlatie et al. (2005) and it is not repeated in this study. According to Pihlatie et al. (2005), the area contributing 85% to the EC flux lies within 60 m (x/h_c=2.4) around the measurement mast.

At Kalevansuo site footprint functions for passive tracers released from the forest floor were calculated with the forward Lagrangian stochastic model as described by Rannik et al. (2000, 2003). The model predicted the horizontal distribution of the surface sources of the flux measurements for three selected wind direction (WD) sectors (140°<WD<190°, 190°<WD<240° and 240°<WD<320°) and for two stability classes (near-neutral and unstable conditions, defined for values of $|L|>200$ and $-200<L<0$ respectively, where L is the Obukhov length measured above canopy). As fluxes and characteristics of turbulence were measured only at two heights – one within the canopy and one above – the forms of the profiles of flow statistics were adopted from the work by Rannik et al. (2003). However, to account for the actual flow characteristics the profiles were scaled to go through the present observations.

Estimated footprint functions were rather similar for different wind direction sectors and they show a rather small influence of stability conditions at the sub-canopy reference height z/h_c=0.25 (Fig. 3). The upwind distance x corresponding to 85% of cumulative footprint values is about 30 m (x/h_c=1.87).

4.3 Co-spectra

Empirical co-spectral model (Eq. 1) was fitted to the sensible heat co-spectra, measured at both sites during daytime conditions. The averaged frequency weighted co-spectra of the sensible heat flux are shown in Fig. 4a and c for Kalevansuo and Sorø respectively, and the fitting parameter values are displayed in Table 2. Prior to averaging operation, it was established that the fitting parameters were not a function of atmospheric stability under near-neutral or unstable daytime conditions.

In the inertial sub-range the sensible heat flux co-spectra $\mathrm{Co}_{w\theta}$ measured within the canopies are less steep than the expected surface layer slope −7/3 (−2.33) (Kaimal et al., 1972), and the transfer of energy from the production to the dissipation scales follows a slope equal to about −1.94 for Sorø and −2 for Kalevansuo (Table 2). Similar result was obtained by Amiro et al. (1990) inside three different types of forest canopies (aspen, pine and spruce). The average value of the normalized frequency n_m is smaller for Sorø (0.073) than the one estimated for Kalevansuo (0.12). This difference is likely due to the different height of the canopies. In the roughness sub-layer the scalar transport is dominated by coherent structures (ejection-sweep cycle), whose typical length scales are proportional to the canopy height h_c (Kaimal and Finnigan, 1994). Hence the difference in n_m between the two sites could be explained just defining a new normalized frequency $n_{mh}=n_m h_c/z$. Using the canopy height h_c instead of the measurement height z, the normalized frequency values at which the co-spectra peak become equal to 0.6 for both sites, which indicates that the most energetic eddies scale with h_c. While such a simple co-spectral model described very well the sensible heat co-spectra measured during daytime, it was found unsuitable for fitting the night-time measured co-spectra, which were often characterized by larger uncertainty as result of multi-scale non-stationary processes usually affecting the night-time scalar transport in the sub-canopy layer (Cava et al., 2005).

The N_2O co-spectra show more random variability especially in the low frequency range, where contributions with opposite direction to the total covariance are measured and the effect of N_2O signal drift is clearly evident. Instead at higher frequencies the N_2O co-spectra behave similarly to the sensible heat, except that they show a damping effect at the end of inertial sub-range, as discussed in the following Sect.

4.4 Flux systematic error

Systematic flux underestimation due to the system characteristics results from physical limitations in the sensor response times, separation distances between the sonic probe and the gas inlet, size of the sensors, the use of sampling line filters, and the sampling tube dimensions. Therefore, these limitations concern mainly the high frequency band of the scalar fluctuations. All mentioned effects could be described quantitatively by transfer functions according to Moncrieff et al. (1997) and Aubinet et al. (2000) and the flux loss can be estimated by using co-spectral correction method (Moore et al., 1996; Horst, 1997; Eugster and Senn, 1995). In order to assess the applicability of this method in the sub-canopy layer, we simulated first the high frequency loss of CO_2 flux, whose measured co-spectra show less random uncertainty than those of N_2O fluxes. At Kalevansuo site the CO_2 flux loss is mainly due to the separation distance between the sonic probe and the head of Licor 7500. The effective first-order transfer function was also experimentally estimated as a ratio between the measured normalized co-spectrum of the CO_2 and sensible heat flux (Mammarella et al., 2009). The normalizing factors were calculated over frequencies not affected by attenuation (Aubinet et al., 2000). Figure 5 shows the predicted and measured CO_2 co-spectra calculated during daytime and a typical mean value of sub-canopy wind velocity of $0.7\,\mathrm{m\,s^{-1}}$. Here the predicted co-spectra for CO_2 refer to the normalized temperature co-spectrum damped either by using the effective transfer function and the theoretical ones according to Moncrieff et al. (1997). In all analysed cases, both methods were suitable for estimating the CO_2 flux loss, which was about 5%. Despite the fact that the within canopy turbulence at small scale likely is not isotropic, the high frequency flux loss during daytime conditions was rather well simulated and predicted by using co-spectral correction methods.

In the case of the TDL-EC system, the spatial separation between the sonic probe and the gas inlet together with the TDL sampling cell response time cause the largest part of the high-frequency underestimation. Although the N_2O co-spectra measured at both sites are remarkably noisier than the previously shown CO_2 co-spectrum, the damping of the highest frequencies for Kalevansuo is broadly predicted by the sensible heat co-spectra attenuated by the appropriate transfer functions (Fig. 6a). For Sorø site (Fig. 6b) the measured N_2O co-spectrum surprisingly does not show similar damping at the high frequency end. Besides the random uncertainty of co-spectral density estimate, such behaviour is likely partly related to the EC digital filter of TDL system used during the Sorø campaign. In fact the corresponding N_2O spectrum showed an "apparent" −5/3 inertial sub-range at high frequency end (not shown), where we would expect a signal dominated by white noise. The resulting flux reduction was less than 10% for both sites.

4.5 Flux random uncertainty

Random flux error of N_2O and sensible heat flux measurements were estimated according to Eq. (2) for Kalevansuo and Sorø datasets.

Figure 7a, b shows the frequency distribution of relative flux error $\Delta F = \delta F/F$, where F is the flux value calculated over the averaging period T=30 min. The relative flux error for N_2O flux is larger than the one estimated for sensible heat flux. In case of N_2O fluxes the relative errors are larger for negative flux values. This result indicates statistically less significant values in case of downward fluxes.

In evaluation of average flux statistics classification according to some threshold value of relative flux error is done. For example, by using $|\Delta F|<1$, which means that for such subset the fluxes are with probability 68% within one standard deviation from the mean, as criterion to select the fluxes with higher confidence level (i.e. with smaller random errors), the frequency distribution of N_2O flux values changes (less downward fluxes) as shown in Fig. 7c, d. However we should acknowledge that the soil N_2O uptake seems not merely a result of random stochastic effect of flux values, as approximately 38% of 30 min downward fluxes for Kalevansuo and 12% for Sorø are statistically significant (larger than the estimated random flux error δF). On the other hand, it is worth to mention that occasional or constant N_2O uptake in forest and agricultural soils have been also previously reported in literature (e.g. Goossens et al., 2001; Butterbach-Bahl et al., 1998; Rosenkranz et al., 2006; Pihlatie et al., 2007; Chapuis-Lardy et al., 2007; Neftel et al., 2007).

4.6 Comparison with chamber fluxes

For validation purpose, N_2O fluxes measured by the EC technique were compared to the soil N_2O emission values simultaneously measured by automatic chambers during the field campaigns (see Pihlatie et al., 2005; 2009). Chambers were located 50 meters northwest and 100 meters southwest from the sub-canopy EC mast for Sorø and Kalevansuo site respectively.

Both of the measurement sites have limitations in a true method comparison between the EC and chamber fluxes. In the Kalevansuo the automatic chambers were located slightly outside the estimated footprint area of the EC system (see Sect. 4.3 and Fig. 3). However, as the vegetation around both the automatic chambers and the sub-canopy EC mast was very similar, we can relatively reliably compare the fluxes obtained by these two methods. In Sorø, the automatic chamber was well within the footprint area of the EC system, however, as there was only one big automatic chamber, the comparison between the two methods is uncertain due to the high spatial variability in N_2O emissions at the measurement site (Pihlatie et al., 2005).

In order to smooth out the run-to-run variability and further reduce the flux random uncertainty, it is a common procedure to compare ensemble averaged flux statistics.

Comparison of daily mean values of EC and automatic chamber fluxes for Sorø and Kalevansuo are reported in Fig. 8. Top panels show EC fluxes calculated after applying a standard linear detrending operation to 30 min runs of N_2O and vertical wind velocity signals (EC-LDT). In middle panels a recursive high pass filter with a time constant equal to 50 s was applied prior flux calculation (EC-RMF). For Kalevansuo site EC-LDT fluxes are randomly distributed around zero, showing a large variability, which is mainly due to the N_2O signal drift. The Sorø EC-LDT fluxes show less random variability, but unexpected N_2O uptake for some days. The randomly large values are significantly reduced in EC-RMF fluxes (especially in Kalevansuo), which are comparable with the magnitude of chamber fluxes. A comprehensive analysis of temporal variability of N_2O emission and environmental driving factors is reported in Pihlatie et al. (2005) for Sorø and Pihlatie et al. (2009) for Kalevansuo site.

Mean and median values of EC fluxes calculated over the entire campaign periods with different methods (LDT or RMF) and selected according to confidence level criteria (ΔF) are compared with the automatic chambers flux statistics (Tables 3 and 4). In most of the cases the mean and median values of EC fluxes were smaller than the corresponding values by the automatic chamber (AC) technique, however showing a larger statistical uncertainty and dispersion as indicated by the mean standard error (stde) and the 25th/75th percentile values respectively. The EC flux statistics from the distribution of 30 min flux calculated by LDT method show the largest departure from the AC flux statistics. For Kalevansuo dataset the LDT based estimate of N_2O emission in $\mu g\,N\,m^{-2}\,h^{-1}$ was 1.13 (stde=1.38) as mean value and 1.28 (25th/75th percentiles=−5.14/8.73) as median value, while the corresponding statistics for Sorø were 4.01 (stde=1.2) and 3.44 (25th/75th=1.1/7.2). The weak significance of LDT flux statistics is due to randomly large values frequently observed (especially for Kalevansuo) during periods characterized by low frequency variability in N_2O concentrations, mainly due to the instrumental drift. The RMF method reduces the scatter and random variability of the fluxes, and at the same time producing an increase of the estimated average N_2O emission, which is notable in Kalevansuo and relatively small in Sorø dataset. Again this suggests stronger effects of optical interference fringes during Kalevansuo campaign.

For further validation and comparison purpose, the measured 30 min fluxes were conditionally selected according to the estimated values of ΔF. Here we used a threshold, $|\Delta F|<1$, noting that for a Gaussian distribution 68% of data values lie within $\pm 1\sigma$ of the mean. Despite the fact that 30 min downward N_2O fluxes are only partly removed by such criterion (Sect. 4.5), at both sites ensemble EC flux statistics get closer to the whole period net flux values estimated by automatic chamber technique (Tables 3 and 4).

5 Conclusions

Eddy covariance measurements of N_2O fluxes with today's commercially available trace gas analyzers for N_2O still are a special challenge, and careful consideration of instrument performance is needed. Moreover, for this case study, the special conditions of turbulent flow inside a plant canopy require an in-depth assessment of the data obtained. The focus of this paper was thus on quality control aspects related to data processing as well as an error analysis related to flux sampling. With respect to data processing, the results shown here highlight that fringe effects in the N_2O signal, measured by TDL spectrometers (TGA100 and TGA100A, Campbell Scientific Inc.), have strong impact on the data quality of the N_2O EC flux values. Although an active thermal control of the TDL enclosure in theory could help to partially eliminate this effect (Billesbach et al., 1998), further tests in the field are needed to assess the efficacy of it. On the other hand, this case study of eddy covariance measurements has demonstrated that signal processing strategies still are a key issue to assure the quality of trace gas flux measurements based upon such complex systems (Werle et al., 2004). In this context, the concept of the Allan variance is a valuable tool to characterize system stability and in the time domain it provides similar information as spectral analysis in the frequency domain (Werle et al., 2008). It was found that during post sampling data processing a high-pass filter time constant of 50 s was able to reduce the fringe effect. The LDT method and RMF method with time constant >100 s (not shown here) lead to increased scatter and/or random uncertainty in fluxes during periods characterized by low frequency variability in concentrations, mainly due to instrument drift.

Flux error analysis, traditionally used in the micrometeorological community for energy and CO_2 fluxes, has been applied to N_2O flux measurements, in order to identify uncertainty of fluxes caused by instrumentation problems and systematic as well as random errors. Although for our EC sub-canopy systems systematic errors due to low pass filter effects of measured fluxes were rather small, we demonstrated that the co-spectral transfer function method is a suitable approach for correcting fluxes measured within canopy layer. EC N_2O flux measurements showed larger random uncertainty than the other measured EC fluxes, and classification according to statistical significance of single flux values indicates that downward N_2O fluxes have larger random error. Finally we demonstrated that the estimated RMF fluxes show less scatter and random variability, and they are in good agreement with the N_2O efflux estimated by the automatic soil chambers.

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Table 1. The setup details of the two EC-TDL systems.

Site	Kalevansuo	Sorø
Sonic anemometer	CSAT3 – Campbell	Solent 1012 – Gill
N_2O analyser	TGA 100 A – Campbell	TGA 100 – Campbell
CO_2 and H_2O analyser	Li-Cor 7500	–
Inlet height	4 m	3 m
N_2O sampling tube	PE aluminium composite (synflex 1300)	PTFE Teflon
Length	4 m	10 m
Outer/inner diameter	9.75 mm/4.25 mm	6 mm/4 mm
Dryer	142 cm Nafion dryer (PD1000, Perma pure Inc.)	142 cm Nafion dryer (PD1000, Perma pure Inc.)
Sample cell (length)	1.5 m	1.5 m
– volume	480 ml	480 ml
– flow	15 slpm	14 slpm
– pressure	50 mbar	70 mbar
– sampling cell response time (effective bandwidth)	0.095 s (1.67 Hz)	0.14 s (1.12 Hz)
Spatial separation between sonic probe and N_2O inlet	0.15 m	0.1 m
Pump	Busch rotary-vane pump (RB0021-L)	Busch rotary-vane pump (RB0021-L)
Reference gas	2000 ppm in reference cell	2000 ppm in reference cell

Table 2. Fitting parameter values of co-spectral model (Eq. 1) applied to sub-canopy sensible heat co-spectra measured during daytime at Kalevansuo and Sorø site.

Parameters	m	Inertial sub-range slope $(m+1)$/m	μ	n_m
Kalevansuo	1.004	2	0.84	0.122
Sorø	1.06	1.94	1.02	0.07

Table 3. Mean and median fluxes of N_2O measured by eddy covariance (EC) and automatic chambers (AC) in Kalevansuo during 25 April–26 June 2007. All fluxes are in $\mu g\,N\,m^{-2}\,h^{-1}$.

Kalevansuo	Mean (stde)	Median (25th/75th perc)
N_2O_EC (LDT)	1.13 (1.38)	1.28 (−5.14/8.73)
N_2O_EC (RMF)	3.24 (0.5)	2.54 (0.2/5.1)
N_2O_EC ($\|\Delta F\|<1$)	4.59 (0.96)	4.33 (0.32/7.1)
N_2O_AC	4.53 (0.03)	4.22 (3.28/5.04)

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 4. Mean and median fluxes of N2O measured by eddy covariance (EC) and automatic chambers (AC) in Sorø during 3 May–31 May 2003. All fluxes are in $\mu g\,N\,m^{-2}\,h^{-1}$.

Sorø	Mean (stde)	Median (25th/75th perc)
N_2O_EC (LDT)	4.01 (0.3)	3.44 (1.1/7.2)
N_2O_EC (RMF)	4.79 (0.7)	3.61 (2.5/5.1)
N_2O_EC ($\lvert\Delta F\rvert<1$)	7.2 (0.4)	5.33 (3.8/8.0)
N_2O_AC	9.85 (0.12)	9.6 (7.55/12.53)

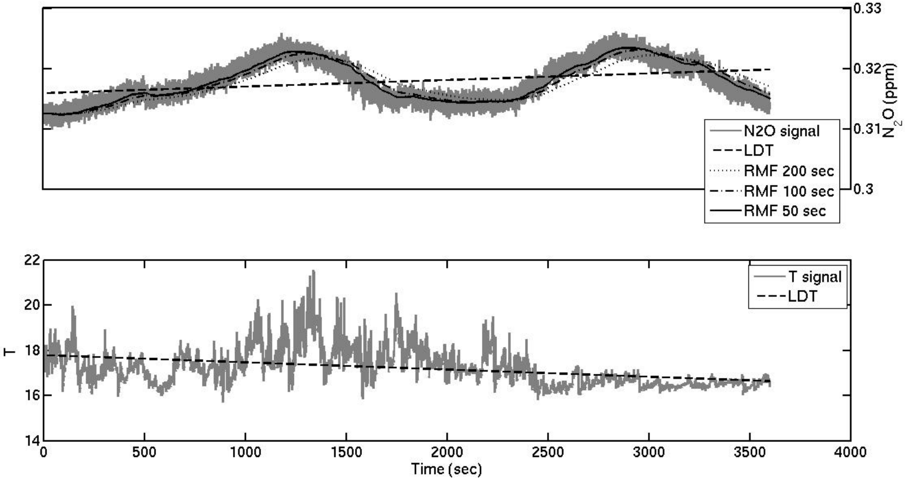

Fig. 1. Example of 1 hour timeseries (18 May, 15:00–16:00 h) of N_2O concentration measured by TGA-100A at Kalevansuo site, showing the effect of optical interference fringes (upper panel). The sonic temperature signal is also displayed for comparison (bottom panel).

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

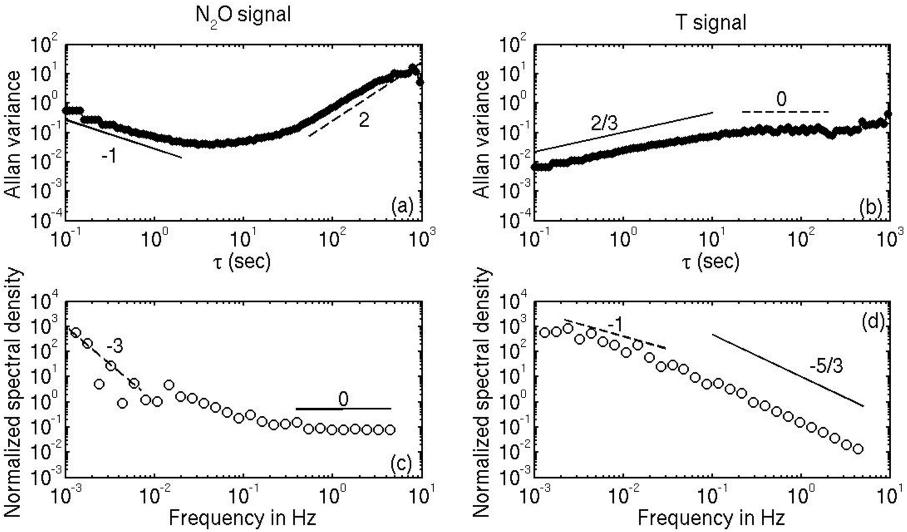

Fig. 2. **(a)** and **(b)** Allan variance plot of N_2O and sonic temperature timeseries displayed in Fig. 1. **(c)** and **(d)**: The corresponding normalized spectral densities. Lines show the slope of different domains characterizing the signals (see the text).

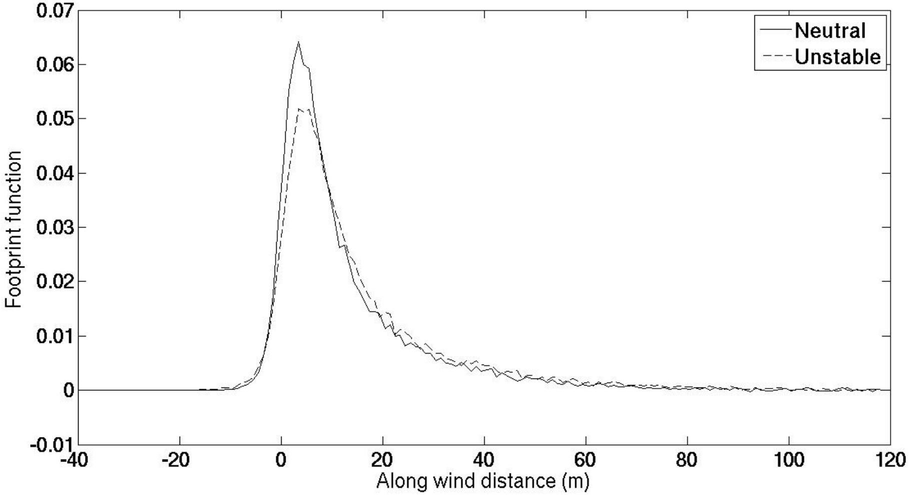

Fig. 3. Flux footprint function as a function of along wind distance estimated for Kalevansuo site. Sources are at the forest floor and the observation height is 0.25 h_c.

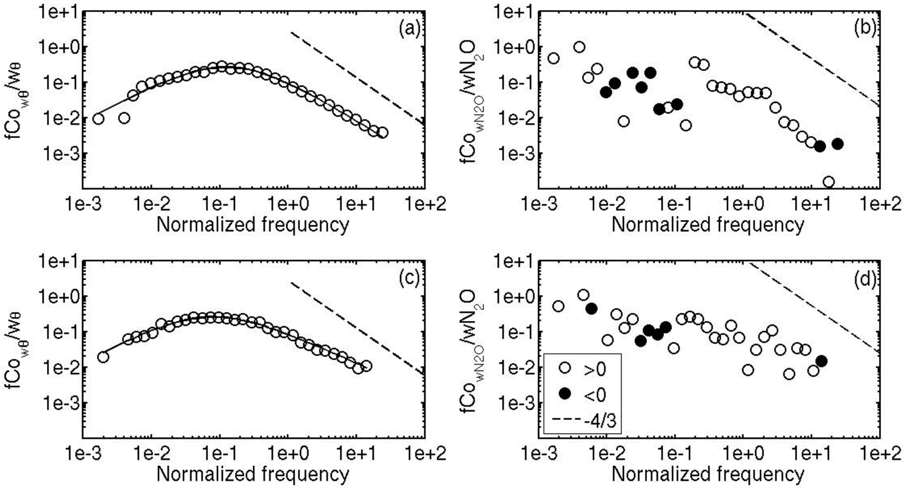

Fig. 4. Ensemble averaged co-spectra of sensible heat and N_2O fluxes measured under unstable stratification during the Kalevansuo (**a** and **b**) and Sorø (**c** and **d**) campaigns. The wind velocity was $0.8\,m\,s^{-1}$ and $0.6\,m\,s^{-1}$ for Kalevansuo and Sorø respectively. The solid line is the fitted co-spectral model (Eq. 1) and dashed line indicates the theoretical inertial sub-range slope.

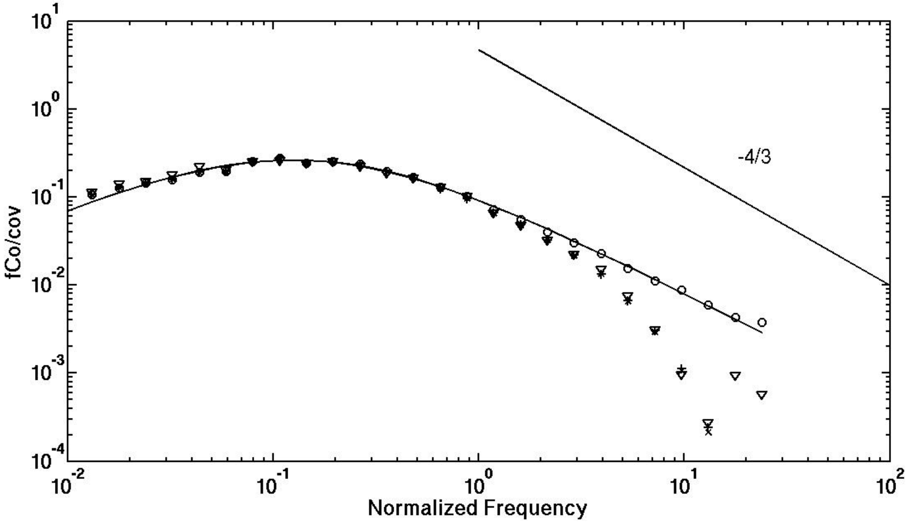

Fig. 5. Example of normalized co-spectra of sensible heat (open circle) and carbon dioxide (open down triangle) fluxes measured under unstable stratification during the Kalevansuo campaign. The solid curve is the fitted co-spectral model (Eq. 1) and the plus and cross symbols are the predicted CO_2 co-spectra computed by multiplying the co-spectral model by the theoretical and empirical transfer functions for CO_2 respectively.

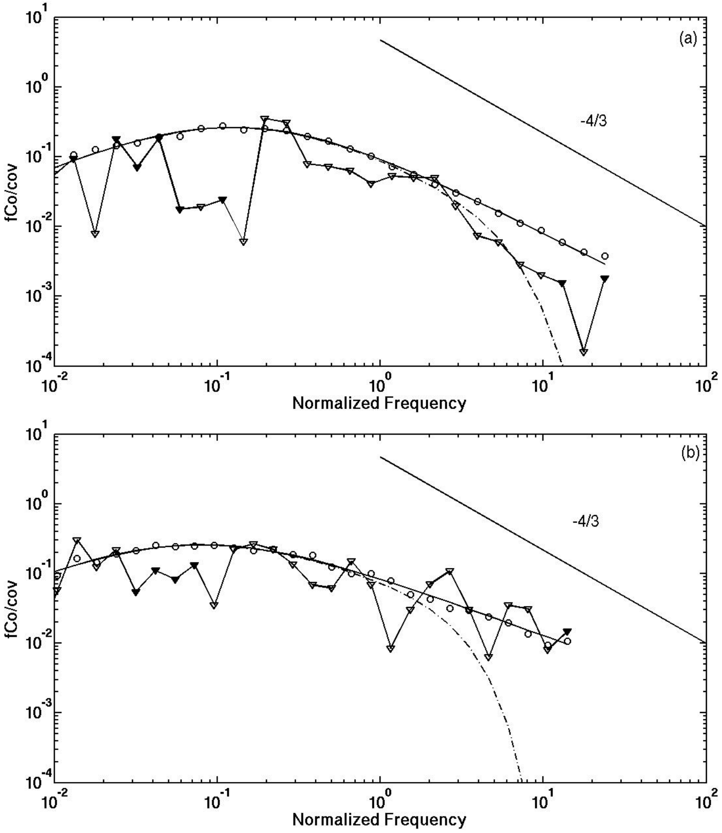

Fig. 6. Example of normalized co-spectra of sensible heat (open circle) and N_2O (down triangle) fluxes measured under unstable stratification during the **(a)** Kalevansuo and **(b)** Sorø campaigns. The solid curve is the fitted co-spectral model (Eq. 1) and the dash-dotted line is the predicted N_2O co-spectra computed by multiplying the co-spectral model by the theoretical transfer function for N_2O.

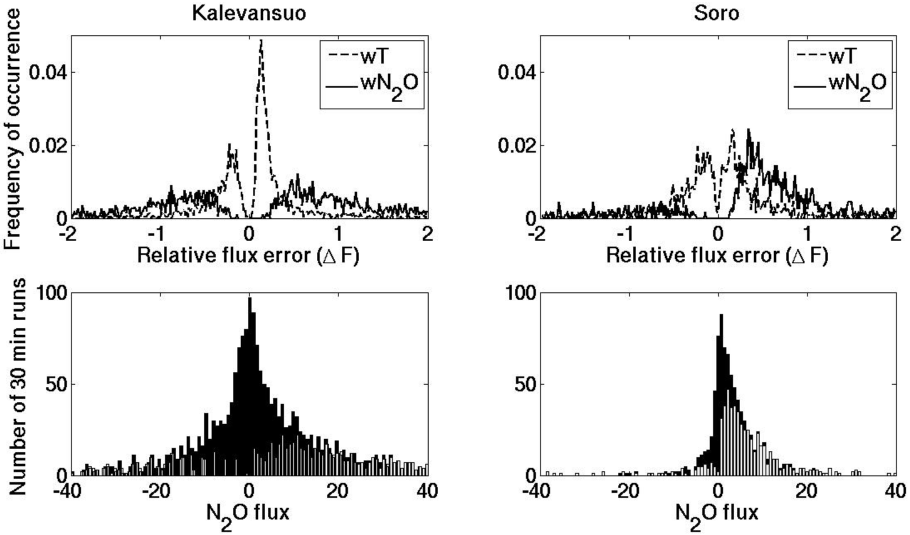

Fig. 7. The distribution curves of the relative flux error as estimated by $\delta F/F$ for sensible heat and N_2O fluxes ($\mu g\,N\,m^{-2}\,h^{-1}$) for **(a)** Kalevansuo and **(b)** Sorø datasets. Panels **(c)** and **(d)** show the histograms of 30 min N_2O fluxes prior (black bar) and after (grey bar) the random flux error criterion $\Delta F < 1$.

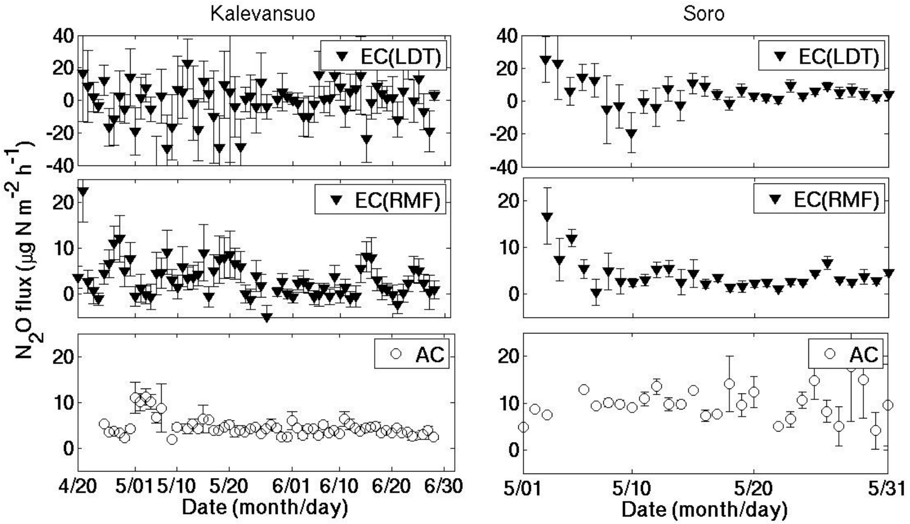

Fig. 8. Daily mean of N_2O fluxes measured by eddy covariance (top and middle panels) and automatic chambers (bottom panels) during April–June 2007 at Kalevansuo pine forest and during May 2003 at Sorø beech forest. Eddy covariance fluxes are calculated by using linear detrending (EC-LDT) and running mean filter (EC-RMF). Error bars stand for standard error of the mean.