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Suitability of quantum cascade laser spectrometry for CH_4 and N_2O eddy covariance measurements

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Abstract

A quantum cascade laser spectrometer was evaluated for eddy covariance measurements of CH_4 and N_2O using laboratory tests and three months of continuous measurements. Moreover, an indication was given of CH_4 and N_2O exchange. All four required criteria for eddy covariance measurements related to continuity, sampling frequency, precision and stationarity were checked. The system had been running continuously at a dairy farm on peat grassland in the Netherlands from 17 August to 6 November 2006. An automatic liquid nitrogen filling system was employed for unattended operation of the system. A sampling frequency of 10 Hz was obtained using a 1 GHz PC system. A precision of 2.6 and 0.3 ppb $Hz^{-1/2}$ was obtained for CH_4 and N_2O, respectively. However, it proved to be important to calibrate the equipment frequently using a low and a high standard. Drift in the system was removed using a 120 s running mean filter. Average fluxes and standard deviations in the averages of 484±375 ngC $m^{-2}s^{-1}$ (2.32±1.80 mg $m^{-2}h^{-1}$) and 39±62 ngN $m^{-2}s^{-1}$ (0.22±0.35 mg $m^{-2}h^{-1}$) were observed. About 40% of the total N_2O emission was due to a fertilizing event.

1 Introduction

The greenhouse gasses Methane (CH_4) and Nitrous oxide (N_2O) play a major role in global warming with global warming potentials 21 and 310 times greater than CO_2, respectively (IPCC, 2001). Agricultural soils are major sources of both gasses (IPCC, 2006). However, there are significant uncertainties in the estimated CH_4 and 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 obtain the emissions. High-frequency micrometeorological methods are often used to obtain integrated emission estimates on a hectare scale that also have continuous coverage in time. Convenient instrumentation is now becoming available that meet

the requirements for eddy covariance (EC) operation. For example, a limited number of eddy correlation measurements have been published using lead salt tunable diode laser spectrometers (TDL), but these often suffer from drift and insensitivity effects (e.g. Smith et al., 1994; Wienhold et al., 1994; Laville et al., 1999; Hargreaves et al., 2001; Werle and Kormann, 2001).

Quantum cascade laser spectrometers (QCL) are more stable and sensitive instruments compared to TDL-systems. QCL spectroscopy was first demonstrated in 1994 (Faist et al., 1994). Detailed descriptions of the working principles of QCL are given in Nelson et al. (2002) and Jiménez et al. (2005). Nelson et al. (2004) pointed out that the instrument must satisfy four criteria for performing CH_4 and N_2O EC-measurements. First, a precision of about 4 ppb and 0.3 ppb is required for CH_4 and N_2O at average ambient concentrations of 1800 ppb and 320 ppb, respectively. Second, the drift should be minimal during a period of atmospheric stationarity on the order of 30 min. Third, the measurement frequency should be in the order of 10 Hz (Monteith and Unsworth, 1990) to evaluate the small eddies as well. Finally, the instrument should operate on a continuous basis. Nelson et al. (2004) showed that quantum cascade lasers can meet these criteria. However, this conclusion is mainly based on technical and theoretical considerations. Therefore, it is desirable to perform practical tests to validate the suitability of a QCL for EC-measurements.

This paper discusses the performance of the QCL for EC-measurements using laboratory tests and three months of continuous measurements at a dairy farm on peat grasslands in the Netherlands. Moreover, an indication will be given of CH_4 and N_2O emissions behaviour during these months. A description of the experimental site and the climatic conditions is given in Sect. 2. Section 3 is devoted to the instrumentation and the methodology. The results are shown in Sect. 4. Finally, the conclusions and discussions are presented in Sect. 5.

2 Experimental site and climatic conditions

The measurements were performed at an intensively managed dairy farm. This farm is located at Oukoop near the town of Reeuwijk in the Netherlands (Coord N 52°01′15″, E 4°01′17″). The surrounding area of the measurement location has soil consisting of a clayey peat or peaty clay layer of up to 25 cm on up to 12 m eutrophic peat deposits. Rye grass (Lolium perenne) is the most dominate grass species with rough bluegrass (Poa trivialis) often co-dominant. Clover species constitute less than 1% of the vegetation (Veenendaal et al., 2007[1]). About 21% of the area is open water (Nol et al., 2007[2]). The mean elevation of the polder is between 1.6 and 1.8 m below sea level. Ditch water level in the polder is being kept at –2.39 in winter and –2.31 m in summer (Veenendaal et al., 2007[1]). The climate is temperate and wet, with an average temperature of 10.3°C in 2004 and 2005, and with an average annual precipitation of about 870 mm in 2004 and 2005. The dominating wind direction is southwest (Veenendaal et al., 2007[1]). A summary of the main characteristics is given in Table 1.

Manure and fertilizing are applied from February to September. Manure and artificial fertilizing application were about 55 $m^3\,ha^{-1}yr^{-1}$ (253 $kgN\,ha^{-1}yr^{-1}$) and 320 $kg\,ha^{-1}yr^{-1}$ (84 $kgN\,ha^{-1}yr^{-1}$) in 2006. Continuous CH_4 and N_2O EC-measurements (coverage of 87%) had been performed from August 17th to 6 November 2006. The averaged temperature over the measurement period was 17°C and 55 $kgN\,ha^{-1}$ cow manure was applied on 14 September 2006.

[1] Veenendaal, E. M., Kolle, O., Leffelaar, P., et al.: Land use dependent CO_2 exchange and carbon balance in two grassland sites on eutropic drained peat soils, Biogeosci. Discuss., submitted, 2007.

[2] Nol, L., Verburg, P. H., Heuvelink, G. B. M., and Molenaar, K.: Effect of land cover data on N_2O inventory in fen meadows, J. Environ. Quality, submitted, 2007.

3 Instrumentation and methodology

The four required criteria for performing EC-measurements of CH_4 and N_2O were validated using laboratory tests and three months of field measurements. The laboratory tests consisted of concentration measurements to evaluate precision, stationary and sampling frequency. The field measurements consisted of three months of continuous EC-measurements with which the continuity of the system was checked and a first indication of the CH_4 and N_2O exchange was obtained.

3.1 Instrumentation

The QCL was placed in a container of 2×2×2 m at about 20 m east from the mast. The measurement height was 3m and the mast was positioned in the middle of the field. Terrain around the towers was flat and free of obstruction for at least 600 m in all directions, except for the container. Wind speed, air temperature, CH_4 and N_2O concentrations were measured with a system consisting of a three-dimensional sonic anemometer (model R3, Gill Instruments, Lymington, UK) and a quantum cascade laser spectrometer (model QCL-TILDAS-76, Aerodyne Research Inc., Billerica MA, USA).

The QCL has a multi-pass cell with an optical path of 76 m and a volume of 0.5 l maintained between 15 and 40 Torr. The QCL has two laser positions available that can be used simultaneously. During these experiments only one laser was used which operated at the 1270 and 1271 cm^{-1} absorption lines for CH_4 and N_2O, respectively. The laser was used in pulsed mode. A sequence of laser light pulses, each with duration of about 10 ns, is divided by a beam splitter and sent through the multi-pass cell and along a bypass. Both beams are detected on a single detector sequentially with the bypass pulse arriving 250 ns before the multi-pass pulse. The laser frequency is tuned through the absorption lines using a sub-threshold current applied to laser between pulses. The laser light intensity is lower at the start of the pulse sequence at about 1269 cm^{-1} and increases towards the end of the pulse sequence at 1272 cm^{-1}.

This is true for both beams. The bypass signal is used to normalise the signal obtained from the multi-pass cell. The result is a pattern that shows a relatively constant intensity ratio with a decrease in light intensity passing through the multi-pass cell at the frequencies of the two absorption lines.

The QCL-software uses spectral parameters listed in the HITRAN database to make a fit to this pattern and derive approximate CH_4 and N_2O gas concentrations (Rothman and Barbe, 2003). With pulsed-QCLs, the laser line width is on the same order as the Voigt line width of the absorber, and therefore must be considered in the fitting routine by convolving the laser line shape with the molecular absorbance. The non-Gaussian shape of the laser line profile can result in underestimating the molecular concentration from 10 to 20% depending on the line depth. Calibration with known standards is therefore necessary for greater accuracy. A more detailed description of the QCL is found in Nelson et al. (2002) and Jiménez et al. (2005).

The detectors of the QCL spectrometer require cooling by liquid nitrogen for maximum sensitivity in the wavelength region. The 0.5 l dewar on the optical table needs to be refilled approximately every 24 h. An automated filling unit was used (with a 50 l storage dewar produced by Norhoff, Netherlands). With this setup visits to the instrument were necessary only once a week. In order to minimize drift owing to changing alignment the temperature cover and optical table were maintained at 35±0.1°C by thin film heaters. The laser electronics were stabilized at ±0.1°C using circulating water bath Nelson et al. (2004). Otherwise, a variation in reported mixing ratios can occur when ambient temperature surpasses the system temperature as large as 2 ppb°C^{-1} for N_2O (Nelson et al., 2004).

The air inlet was located at the sonic height of 3 m above the field. A 25 m PTFE inlet tube with a diameter of 0.25 inch was used. At the QCL inlet a 0.01 µm filter (DFU filter tube grade BQ, Balston, USA) was used to avoid degradation of the multi-pass cell mirrors. The flow and cell pressure were controlled with a needle valve at the inlet of the multi-pass cell. A vacuum pump (TriScoll 600, Varian Inc, USA) with a maximum volume flow rate of 400 l min^{-1} was located downstream of the multi-pass cell. The QCL

was calibrated at least once a week using mixtures in N_2/O_2 of 1700 and 5100 ppb for CH_4 and 300 and 610 ppb for N_2O (Scott speciality gasses, Netherlands)

The sonic anemometer data and the QCL-output were logged using the RS232 output and processed using a data acquisition program developed at ECN, following the procedures of McMillen (1988). Both the QCL and the eddy covariance computer were available for remote control. The sampling frequency of the QCL was not exactly uniform. The average time between two samples was about 0.11 s. The sonic anemometer produced an uniform sampling rate of 20.88 Hz. The data acquisition program saved both the QCL and sonic data in the same file at 20.88 Hz using the last measured concentration value. As a consequence, the contribution to CH_4 and N_2O fluxes of large eddies, with sampling frequencies below 5 Hz, were sampled well, but the contribution of smaller eddies were not.

3.2 Methods

The net ecosystem exchange (NEE) of both gasses is given by

$$\underbrace{\int_0^h \overline{S_c} dz}_{\text{NEE}} = \underbrace{\int_0^h \frac{\partial \overline{c}}{\partial t} dz}_{\text{Storage}} + \underbrace{\overline{w'c'}|_h}_{\text{Eddy flux}} \quad (1)$$

when horizontal homogeneity, stationarity and a flat terrain are assumed. The NEE consists of the sources, sinks and surface flux (e.g. based on Hoogendoorn and van der Meer, 1991 and Nieuwstadt, 1998).

Evaluation of the eddy flux consisted of different phases. First, the raw data of $w(t)$ and $c(t)$ was analyzed by eye on spikes and malfunctioning. Then, all concentration data was corrected using a two-point calibration factor based on weekly calibrations. The standards were 1700 and 5100 ppb for CH_4, and 300 and 610 ppb for N_2O (Scott speciality gasses, Netherlands). The two-point calibration factor f_{LH} is defined by

$$f_{LH} = \frac{S_H - S_L}{M_H - M_L} \quad (2)$$

in which S_L and S_H are the low and high standard values in ppb and M_L and M_H are the low and high measured values in ppb. The corrected concentration was found using this factor and the following equation

$$C_{cor} = f_{LH} C_{uncor} \tag{3}$$

with C_{uncor} the uncorrected concentration value in ppb and C_{cor} the corrected concentration value in ppb. It was important to correct the data using this factor seeing that the QCL does not provide absolute values for the mixing ratios. Next, the time averaging, which was based on a running mean, and mean removal operations were performed by

$$\tilde{w}_k = (1 - \frac{\Delta t}{\tau_f})\tilde{w}_{k-1} + \frac{\Delta t}{\tau_f} w_k \tag{4}$$

$$\tilde{c}_k = (1 - \frac{\Delta t}{\tau_f})\tilde{c}_{k-1} + \frac{\Delta t}{\tau_f} c_k \tag{5}$$

$$\overline{w'c'} = \frac{1}{n_s} \sum_{k=1}^{n_s} (w_k - \tilde{w}_k)(c_k - \tilde{c}_k). \tag{6}$$

where k is the sampling number, Δt is the interval between two samples in s, τ_f is the running mean filter time constant and n_s is the amount of samples in the averaging period (Lee et al., 2004). The fluxes F_c were calculated using a 120 s running mean filter time constant and a 30-min averaging time. Furthermore, the time lag between the sonic anemometer and QCL-data caused by the length of the sampling tube was determined using the covariance as function of delay time, which is given by

$$F_c = cov_{wc}(n\Delta t) = \overline{w'_k c'_{k+n\Delta t}} = \frac{1}{n_s} \sum_{k=1}^{n_s} w'_k c'_{k+n\Delta t} \tag{7}$$

where the delay time is defined by $n\Delta t$ in which n denotes the amount of time steps. The absolute maximum in covariance, which represents the eddy flux, occurs at the

exact delay time. The exact delay time is dependent on the flow rate in the tube. The flow rate itself is dependent on the resistance of the system, which is mainly dependent on the conditions of the inlet filter. If the inlet filter becomes dirty, the flow rate will decrease. The gradual increase of the resistance of the inlet filter resulted in a slow decrease of the mass flow rate. In our case, the mass flow rates decreased from 22 to 8 standard l min^{-1} and in consequence the delay time increased from 1.5 to 7.6 s. These changes were monitored using the cell pressure. However, the exact delay times were calculated for each day by determining the maximum in covariance of the fluxes.

The Reynolds number for the inlet configuration ranged from about 5020 to 1720 at the high and low flow, respectively. Mixing of air in the inlet tube led to a decreased contribution of the higher frequencies (i.e. the small eddies) to the calculated flux. According to Lenschow and Mann (1994) the damping effect was estimated to be smaller than 50% for frequencies below 3 Hz when cell pressures were above 35 Torr. A thorough investigation on the damping effect could be done using an empirical correction approach given by Ammann et al. (2006). This correction approach is based on the flux ogives which are defined by

$$Og_{wc}(f_m) = \sum_{i=1}^{m} |Co_{wc}(f_i)|$$

$$f_i = \frac{i}{(n_s - 1)\Delta t}; m = 1, 2, \ldots, \left[\frac{(n_s - 1)\Delta t}{2\Delta t}\right] \quad (8)$$

where f represents frequency in Hz and Co_{wc} the co-spectrum. Figure 1 shows the normalized ogives of the CH_4, N_2O and sensible heat flux belonging to 7 October 2006 between 12:00–14:00, which was a neutral period with mean wind velocity of about 7 ms^{-1}. These ogives were determined using block averaging and an averaging time of 30 min. It can be seen that damping effects were almost negligible for this period. Nevertheless, more analyses should be done to investigate the effect of damping on the flux values for all circumstances.

The storage term was calculated using the QCL data according to Eq. (1). The calibration-corrected NEE was given by adding the storage and the eddy flux term. The NEE data were flagged using the instationarity test of Foken and Wichura (1996). Finally, the fetch was checked by a footprint model based on the Kormann-Meixner method (Neftel et al., 2007[3]; Kormann and Meixner, 2001). The 30-min NEE value was rejected when less than 70% of the flux came from the dairy farm site.

4 Results

4.1 Performance EC-measurements

As described by Nelson et al. (2004), an EC-measurement system should satisfy four criteria related to continuity, sampling frequency, precision and stationarity. As for continuity, the system proved to be very stable as far as alignment and laser drift was concerned. The most sensitive part of the system proved to be the liquid nitrogen refilling unit. In summer with high temperatures the container became too hot inside which led to changing alignment. An extra ventilator was installed on the container which proved to be sufficient to keep the temperature inside the container below 35°C. Continuous CH_4 and N_2O EC-measurements (total data coverage 87%) had been obtained from 17 August to 6 November 2006 with about one visit per week excluding the intensive campaigns.

For most conditions a sampling frequency of about 10 Hz is sufficient to perform EC-measurements (Ammann, 1998). According to Nelson et al. (2004) this necessitates both a fast electronic signal processing time and a rapid sampling cell response time. The signal processing time is dependent on the complexity of the spectrum and the number of spectral lines included in the fit. Laboratory tests, using the Aerodyne TDL-Wintel software running on a 1 GHz PC showed that 20 Hz acquisition was possible

[3]Neftel, A., Spirig, C., and Ammann C.: A simple tool for operational footprint evaluations, Environ. Pollut., submitted, 2007.

for 2 or 3 gas species simultaneously. However, the overall frequency response of the system is limited by sampling cell response time rather than the signal processing time. A sampling cell response time (1/e) of τ=0.07 s was obtained using the 400 l min^{-1} Varian Vacuum pump with a cell volume of 0.5 l. This gives an effective bandwidth limitation of $1/(2\pi\tau)\sim$3 Hz which is slightly less than the Nyquist frequency of 5 Hz using a sampling rate of 10 Hz. So, the flux could be underestimated due to to missing contributions of the small eddies by damping effects (see Sect. 3.1, non exactly uniform sampling (see Sect. 3.1) and limited response time.

The system precision and stationarity are strongly dependent on the drift of the instrument. An indication of both properties can be given using an Allan variance analysis (e.g. Allan, 1966; Werle and Slemr, 1991). In this method, the variances in the time series of reported mixing ratio when sampling a constant source from a calibration take are plotted as a function of integration time. The Allan variance decreases with t^{-1} when random noise dominates. This decrease continues to a point at which drift effects start to influence the measurements. Due to instrument drift at longer times the Allan variance increases again. The minimum is indicated by τ_A and σ_A, which represent the stability time in s and the sensitivity in ppb belonging to this stability time. Apart from this, the y-axis intersection point gives an indication of short term precision of the system using

$$\sigma = \sigma_{1s} f_s^{-1/2} \tag{9}$$

in which f_s is the sampling frequency in Hz. Precision and stationarity are determined by drift effects which depend on the instrumental configuration. The most important factor to minimize drift is proper thermal control of optics and the electronics to maintain constant dimensionality and a stable electrical environment of the system. Precision may also be improved by optimizing the least-squares fitting routines to minimize residuals between data and fit, and by optimizing the optical alignment of the system. Optical inference fringes, which can lead to instabilities with continuous wave laser systems, are not as important in pulsed laser systems. However, since the pulsed

laser is operated near threshold to maintain a narrow laser width, the short term precision is generally limited by detector noise. The influence of alignment and therefore the amount of laser power on the detector was investigated using laboratory tests. It was found that the sensitivity was doubled when power at the detector was doubled by alignment optimization. A summary of short term performance for a typical range of operating conditions is given in Table 2.

The minimum in the Allan variance defining the long-term stability which can be reached using this instrument is now about 200 s (Nelson et al., 2004). These results are in agreement with Werle and Slemr (1991) and Wysocki et al. (2005). However, CH_4 and N_2O fluxes are often calculated over an averaging time of 30 min. The choice of this interval is mainly based on the measurement height and the stability of the atmosphere since the size of the contributing eddies depends on those properties. Larger eddies contribute when the measurement height becomes higher and the atmospheric circumstances are more unstable. An overestimation of flux is possibly caused by instrumental drift effects on time scales from 200 s to the longest averaging time of 30 min. This extra contribution only occurs when the fluctuations of the concentration are correlated with the fluctuations of the vertical wind velocity.

A running mean filter is a possible solution to filter drift contributions. Kaimal and Finnigan (1994) suggested a running mean filter with a time constant equal to τ_A. Nevertheless, this filter could cause an underestimation of the flux due to filtering the contributions of large eddies seeing that passive scalars, like CH_4 and N_2O, can acquire mesoscale fluctuations. These mesocale fluctuations can occure while the convective process, which drives their advection, itself fluctuates on a horizontal scale on the order of the boundary layer, i.e. within the microscale range (Jonker et al., 1999). An indication of the underestimation was made by means of ogive analyses based on Lee et al. (2004). The ogives of a neutral period on 7 Oktober 2006 between 12:00–14:00 are given in Fig. 2. These ogives were calculated using a block averaging and an averaging time of one hour.

It was derived that the underestimation due to the 120 s running mean filter was

smaller than 10% during this period. Besides, it was proved that an averaging time of 30 min was long enough in this case. However, more research should be done to derive the amount of underestimation due to the running mean and the minimal required averaging time for all circumstances.

Calibrations have to be performed to improve the accuracy of the mixing ratio values and therefore the accuracy of the flux values. Nineteen calibration sessions were performed during two weeks, these were used for evaluating the difference between low, high and low-high calibrations. The standards were 1700 and 5100 ppb for CH_4 and 300 and 610 ppb for N_2O (Scott speciality gasses, Netherlands). Three different correction factors were calculated a low, a high and a low-high calibration factor. The low-high calibration was defined by Eq. (2) and both other factors were determined by

$$f_L = \frac{S_L}{M_L} \tag{10}$$

$$f_H = \frac{S_H}{M_H}. \tag{11}$$

The corrected concentration was found using one of these factors and the following equation

$$C_{cor} = f_x C_{uncor} \tag{12}$$

with f_x the low, high or low-high calibration factor, C_{uncor} the uncorrected concentration value in ppb and C_{cor} the corrected concentration value in ppb. The average and the standard deviation of the calibrations are given in Table 3.

Table 3 shows a significant difference in all three correction factors. The low-high calibration factor was the best way to estimate the NEE of CH_4 and N_2O. A single point calibration with one-standard can provide flux values that differ by up to 16% from a two-standard estimate. The calibration factor changed when instrument parameters were modified and when changes were made in fitting parameters or in alignment. These kinds of modifications were the main reason for the standard deviation in each of the

factors listed in Table 3. It was also very important to keep the cell pressure constant during the measurement and the calibration, since a pressure change affected the zero offset. This offset was due to a shift in baseline structure. To minimize this effect a better match than 0.1 Torr was required.

4.2 Methane and Nitrous oxide exchange rates

4.2.1 Analysis using 30-min flux values

A dataset of CH_4 and N_2O EC-measurements had been obtained from 17 August to 6 November 2006 for which 99.8% was within the footprint of the investigated dairy farm site. About 7% of the CH_4 and 22% of the N_2O flux values were rejected by the instationarity tests (Foken and Wichura, 1996). However, the averaged standard deviations over six 5-min flux values were 84% and 185% for CH_4 and N_2O, respectively. So, the temporal variation was very large for both greenhouse gases and especially for N_2O. The accepted and calibrated 30-min NEE values are shown in Fig. 3.

In general the measurements for both CH_4 and N_2O show a net emission. About 97% and 86% of all flux values are positive for CH_4 and N_2O, respectively. In consequence, also negative fluxes occurred which is an interesting result, however, the reliability should be analyzed in more detail to investigate if these fluxes were not caused by an instrumental artifact. Most fluxes were between –1000 ngC $m^{-2}s^{-1}$ and 1000 ngC $m^{-2}s^{-1}$ for CH_4 or between –100 ngN $m^{-2}s^{-1}$ and 100 ngN $m^{-2}s^{-1}$ for N_2O. The high positive peaks were clearly related to cow manure application. However, the negative fluxes occurred in short events lasting at most a few hours. The reliability of the fluxes was checked using correlation versus delay time plots, see Fig. 4 for a positive and a negative CH_4 and N_2O flux. These correlation plots suggested that these fluxes were well defined.

Furthermore, the detection limit of the QCL was estimated at 121 ngC $m^{-2}s-1$ and 3 ngN $m^{-2}s^{-1}$ based on the flux of 14 September 2006 21:00 using a method proposed by Wienhold et al. (1995). In this method, the standard deviation of the covariance

function far outside the true lag time is used as the estimation. So, the estimated detection limit was probably most of the time much smaller than the measured CH_4 and N_2O fluxes.

Besides instrumental artifacts, the negative fluxes could be caused by the non-performed Webb-correction (Webb et al., 1980). The Webb-correction for density fluctuations should not apply to our fluxes since there was a constant temperature and pressure in the sampling cell. However, the Webb-correction for the influence of water vapour fluctuations on trace gas fluxes should be applied on the data seeing that the sample was not dried to a constant humidity before the mixing ratio was measured. The average magnitude of the Webb-correction for water vapour may be estimated from the latent heat fluxes. When assuming a maximal and minimal latent heat flux of about 1000 and –400 $W\,m^{-2}$, the maximal Webb-corrections are 484 and –194 $ngC\,m^{-2}s^{-1}$ and 188 and –75 $ngN\,m^{-2}s^{-1}$ for CH_4 and N_2O, respectively. So, a source above 194 $ng\,C\,m^{-2}s^{-1}$ and 75 $ngN\,m^{-2}s^{-1}$ can not change into a sink and a sink below –484 $ngC\,m^{-2}s^{-1}$ and –188 $ngN\,m^{-2}s^{-1}$ can not change through the Webb-correction into a source. An estimation of the corrected fluxes through the Webb-correction was performed using latent heat flux data of the University of Wageningen. These latent heat fluxes were also derived using eddy covariance data at a measurement height of about 3m at the same site. For more information about these measurements the reader is referred to Veenendaal et al. (2007)[1]. Still, 14% and 5% of all fluxes were negative for CH_4 and N_2O after applying this correction.

The conclusion is that large emissions of CH_4 and N_2O occurred at this dairy farm on peat grasslands. Moreover, negative emissions seemed to occur, however, more analyses should be performed to ascertain these uptakes. For the net annual exchange, the uptake episodes were negligible.

4.2.2 Analysis using week flux values

Week average flux values were calculated when data coverage higher than 50% occurred in more than four days a week. An overview of week averaged CH_4 flux and

N_2O flux are presented in Fig. 5. The week average air temperature and the weekly precipitation rates are also shown in Fig. 5. These have been made available by KNMI in the Netherlands. Cow manure was applied in week 37. It can be seen that the highest CH_4 week average also occurred in this week. However, the highest N_2O took place in week 40 after a large amount of precipitation.

4.2.3 Analysis using three months flux values

The average calibration-corrected NEE and the standard deviation in the average were $484 \pm 375\,\mathrm{ngC\,m^{-2}s^{-1}}$ and $39 \pm 62\,\mathrm{ngN\,m^{-2}s^{-1}}$ from which 40% of N_2O emission was due to the fertilizing event. Thus, the standard deviations were of the same order of the average flux values this was mainly caused by the fertilizing event The calibrated NEE was about 25% and 44% higher than the non-calibrated NEE for CH_4 and N_2O, respectively. The average calibration factors over these three months were even higher than the average calibration factors over the nineteen test calibrations, which were performed in two weeks (see Sect. 4.1). This was probably due to changes in temperature and voltage which affected the laser line shape and line width. In consequence, it proved to be very important to calibrate frequently.

The calibrated and Webb-corrected NEE was about 7% higher for CH_4 and 29% higher for N_2O than the calibrated non-Webb-corrected NEE. However, this Webb-correction was based on latent heat fluxes of an open path system which was located at the same height and at a distance of about 3 m from the closed path eddy covariance system of CH_4 and N_2O. In consequence, the Webb-correction should only partially be applied seeing that the 25 m inlet tube of the closed eddy covariance system of CH_4 and N_2O attenuated the fluxes. In consequence, the difference between Webb-corrected and uncorrected would be smaller. Thus, the calibrated NEE values without Webb-correction seemed to be a good first estimation of the CH_4 and N_2O exchange at this dairy farm on peat land. A summary of non-calibrated NEE, calibrated NEE and, calibrated and Webb-corrected NEE is given in Table 4.

5 Conclusions

A quantum cascade laser spectrometer was used for EC-measurements of CH_4 and N_2O. Evaluation of its performance was performed using laboratory tests and three months of field measurements at a dairy farm on peat grasslands in the Netherlands. All four required criteria for EC-measurements related to continuity, sampling frequency, precision and stationarity were first checked in the laboratory. The system was able to run continuously using an automatic liquid nitrogen filling system. A sampling frequency of 10 Hz was obtained using a 1 GHz PC system. A precision of 2.6 and 0.3 ppb $Hz^{-1/2}$ was obtained for CH_4 and N_2O, respectively. However, this precision was strongly dependent on the power on the detector and thus alignment. Two-point calibration was required at least once a week. Drift in the system was removed using a running mean filter of 120 s.

The continuous operation of the system was also proven by three months of field measurements (data coverage of 87%). A first indication of CH_4 and N_2O exchange was made. The average calibrated corrected exchange and its standard deviation was 484 ± 375 ngC $m^{-2}s^{-1}$ and 39 ± 62 ngN $m^{-2}s^{-1}$ from which 40% of N_2O emission was due to the fertilizing event. The N_2O peak, which was strongly correlated to precipitation, occured about three weeks after the fertilizing. Finally, although the dairy farm site was a net source of CH_4 and N_2O, also uptake seemed to occur in short events lasting at most a few hours. However, more research should be done to investigate the reliability of these negative fluxes.

In conclusion, a quantum cascade laser spectrometer was suitable for performing continuous EC-measurements of CH_4 and N_2O. Nevertheless, a two-point calibration was necessary for obtaining accurate estimates. Besides, the possible underestimation due to the damping effect, the use of a running mean filter and the limited effective sampling frequency should be analyzed in more detail.

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Table 1. Main characteristics of Oukoop site in Reeuwijk based on e.g. Veenendaal et al. (2007)[1].

Site	Oukoop in Reeuwijk (NL)
Location	N 52°01′15″ E 4°01′17″
Elevation of the polder (m below sea level)	1.6–1.7
Elevation of the ditches (m below sea level)	2.31–2.39
Height of vegetation (m)	0.15
Mean annual rainfall over 2004 and 2005 ($mmyr^{-1}$)	870
Mean temperature over 2004 and 2005 (°C)	10.3
Cow manure application in 2006 (m^3ha^{-1})	55
Artificial fertilizer application in 2006 ($kgha^{-1}$)	320

Table 2. Measurement precision (ppbHz$^{-1/2}$) for ambient CH_4 and N_2O with a cell pressure of about 60Torr.

	V~80 mV	V~180 mV
CH_4	10	2.6
N_2O	1	0.3

Table 3. Average and standard deviation of nineteen calibration sessions which are performed during two weeks.

Component	f_L [–]	f_H [–]	f_{LH} [–]
CH_4	1.04±0.04	1.14±0.03	1.20±0.06
N_2O	1.03±0.06	1.07±0.05	1.12±0.05

Table 4. Average and its standard deviation of CH_4 and N_2O exchange at a dairy farm in the Netherlands over the period 17 August to 6 November 2006.

	CH_4 [ngC $m^{-2}s^{-1}$]	CH_4 [mg m^{-2} h^{-1}]	N_2O [ngN $m^{-2}s^{-1}$]	N_2O [mg$m^{-2}h^{-1}$]
NEE non-calibrated without Webb-correction	388±275	1.86±1.32	27±42	0.15±0.24
NEE calibrated without Webb-correction	484±375	2.32±1.80	39±62	0.22±0.35
NEE calibrated with Webb-correction	519±400	2.49±1.92	50±68	0.28±0.38

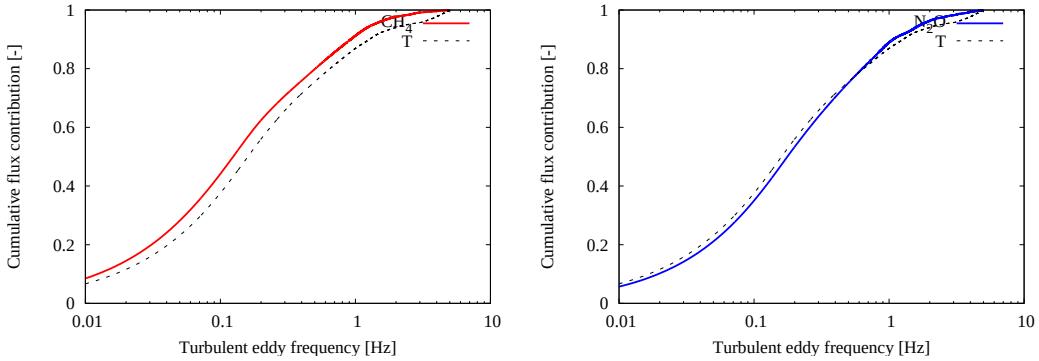

Fig. 1. Comparison of the ogives of the sensible heat and CH_4 flux (left) and of the sensible heat and N_2O flux (right). The given ogives represent averages over 4 half-hourly measurements on 7 Oktober 2006 between 12:00–14:00.

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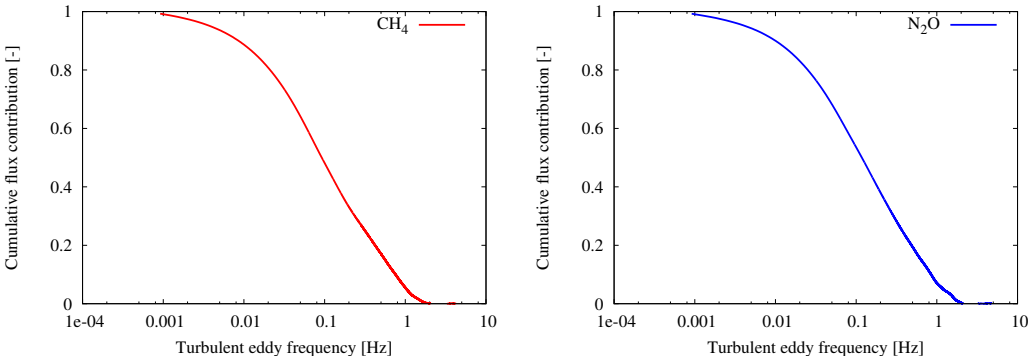

Fig. 2. Ogives of CH_4 flux (left) and N_2O flux (right) for determining the effect of the running mean filter and averaging time. The given ogives represent averages over 2 one-hourly measurements on 7 Oktober 2006 between 12:00–14:00.

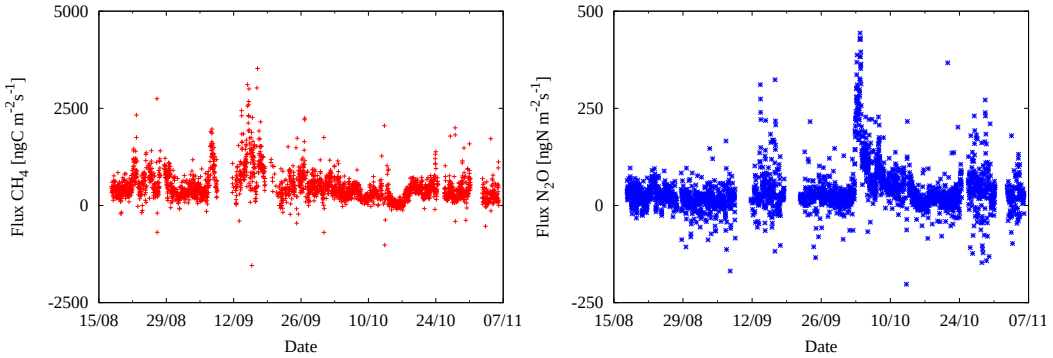

Fig. 3. 30-min flux values of CH_4 (left) and N_2O (right) from a dairy farm site in the Netherlands from 17 August to 6 November.

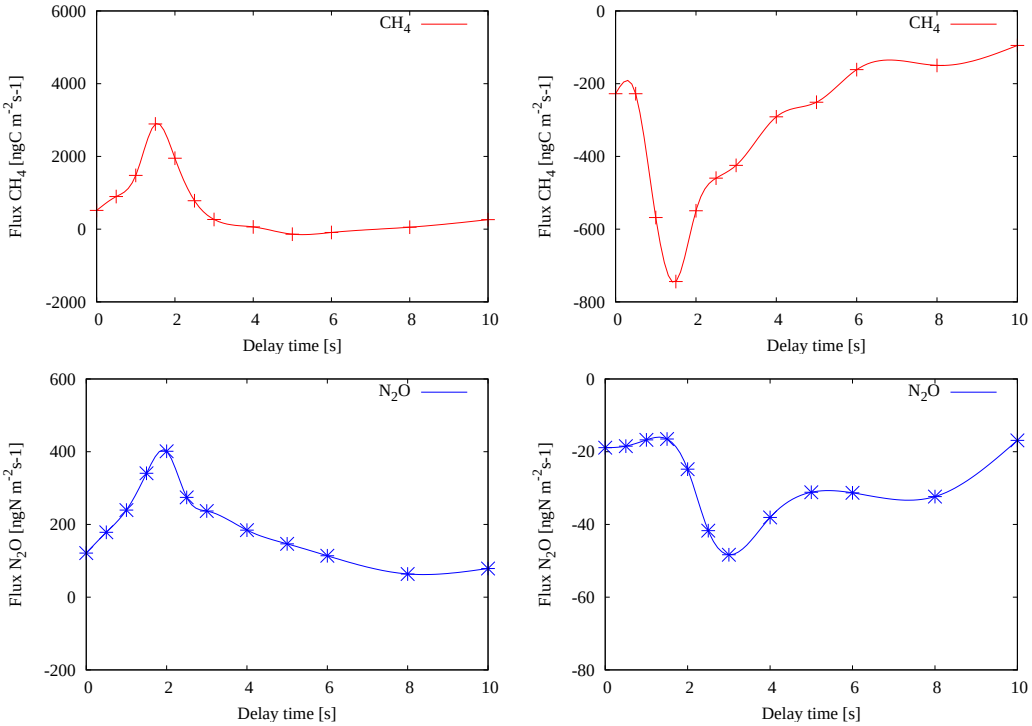

Fig. 4. Correlation versus delay time plots for the positive CH_4 flux of 14 September 2006 21:00 (red crosses) and the positive N_2O flux of 3 Oktober 2006 21:30 (blue stars) in the left figures. Correlation versus delay time plots for the negative CH_4 flux of 23 September 2006 06:30 (red crosses) and the negative N_2O flux of 6 September 2006 13:00 (blue stars) in the right figures.

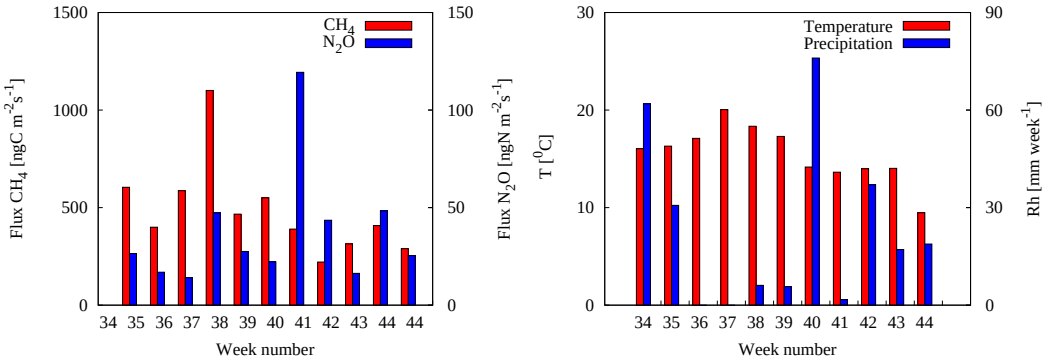

Fig. 5. Week average of CH_4 flux (left columns in red) and week average of N_2O flux (right columns in blue) in left figure and week average of air temperature (left columns in red) and weekly precipitation rates (right columns in blue) in right figure.