Methodical study of nitrous oxide eddy covariance measurements using quantum cascade laser spectrometery over a Swiss forest

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Abstract. Nitrous oxide fluxes were measured at the Lägeren CarboEurope IP flux site over the multi-species mixed forest dominated by European beech and Norway spruce. Measurements were carried out during a four-week period in October–November 2005 during leaf senescence. Fluxes were measured with a standard ultrasonic anemometer in combination with a quantum cascade laser absorption spectrometer that measured N₂O, CO₂, and H₂O mixing ratios simultaneously at 5 Hz time resolution. To distinguish insignificant fluxes from significant ones it is proposed to use a new approach based on the significance of the correlation coefficient between vertical wind speed and mixing ratio fluctuations. This procedure eliminated roughly 56% of our half-hourly fluxes. Based on the remaining, quality checked N₂O fluxes we quantified the mean efflux at 0.8±0.4 µmol m⁻² h⁻¹ (mean ± standard error). Most of the contribution to the N₂O flux occurred during a 6.5-h period starting 4.5 h before each precipitation event. No relation with precipitation amount could be found. Visibility data representing fog density and duration at the site indicate that wetting of the canopy may have as strong an effect on N₂O effluxes as does below-ground microbial activity. It is speculated that above-ground N₂O production from the senescing leaves at high moisture (fog, drizzle, onset of precipitation event) may be responsible for part of the measured flux.

1 Introduction

Water vapor, carbon dioxide, methane, and nitrous oxide are the four most important greenhouse gases in the atmosphere that strongly influence climate and thus also climate change. Whilst water vapor and carbon dioxide flux measurements are now standard within a more or less dense (depending on continent and remoteness) research network of flux stations known as FLUXNET (Baldocchi et al., 2001), in which the European CarboEurope IP network is participating, only few sites are equipped with more difficult to perform methane or nitrous oxide (N₂O) flux measurements. N₂O has the greatest greenhouse forcing potential on a per-molecule basis (Houghton et al., 2001). Still, our knowledge of the individual sources and sinks is poor (Bouwman et al., 1995) and does not adequately cover the large natural variability there is – or is expected – in N₂O fluxes from different ecosystems.

The general knowledge, summarized among others by Meixner and Eugster (1999) is that N₂O is produced mostly in an intermediate soil moisture range where soils are not too dry (which would allow better oxidation of nitrogen, and thus NO emissions) and not too wet and anoxic (which would inhibit oxidation of nitrogen and thus rather lead to N₂ emissions). Since our CarboEurope IP forest site is located on a well-drained mountain slope in the Jura Mountains of Switzerland, it was not known whether N₂O effluxes from this site can safely be neglected in the overall greenhouse gas budget, or whether there is a need to include this component explicitly in our measurement protocol. In this article we report eddy covariance flux measurements obtained during a field test of a newly developed and improved tunable quantum cascade laser absorption spectrometer (QCLAS) during a 4-week period in autumn 2005 at the Lägeren flux site in northern Switzerland. The questions we wanted to answer were: (1) Is this new instrument that does no longer require liquid nitrogen cooling ready for field deployment at FLUXNET locations? (2) Does this technique provide all relevant information that is needed for a thorough assessment of its accuracy for eddy covariance flux measurements? And (3) what is the magnitude of N₂O fluxes from this forest ecosystem and how do they relate to wetting during precipitation events?
Table 1. Tree canopy species composition and above-ground stem wood volumes in the western, the eastern, as well as the total flux footprint area of the Lägeren tower. Data were collected during the winter season 2005/2006.

<table>
<thead>
<tr>
<th>Tree species</th>
<th>English name</th>
<th>West m$^3$ ha$^{-1}$</th>
<th>East m$^3$ ha$^{-1}$</th>
<th>Mean m$^3$ ha$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fagus sylvatica</td>
<td>European beech</td>
<td>59</td>
<td>213</td>
<td>136</td>
</tr>
<tr>
<td>Picea abies</td>
<td>Norway spruce</td>
<td>49</td>
<td>174</td>
<td>112</td>
</tr>
<tr>
<td>Fraxinus excelsior</td>
<td>Ash</td>
<td>146</td>
<td>38</td>
<td>92</td>
</tr>
<tr>
<td>Acer pseudoplatanus</td>
<td>Sycamore</td>
<td>123</td>
<td>35</td>
<td>79</td>
</tr>
<tr>
<td>Abies alba</td>
<td>Silver fir</td>
<td>24</td>
<td>95</td>
<td>60</td>
</tr>
<tr>
<td>Tilia cordata</td>
<td>Linden</td>
<td>36</td>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>Quercus robur</td>
<td>Oak</td>
<td>0</td>
<td>36</td>
<td>18</td>
</tr>
<tr>
<td>Ulmus glabra</td>
<td>Elm</td>
<td>28</td>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>Pinus sylvestris</td>
<td>Scots pine</td>
<td>0</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Prunus avium</td>
<td>Cherry tree</td>
<td>8</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Carpinus betulus</td>
<td>European hornbeam</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Betula pendula</td>
<td>Birch</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sorbus aucuparia</td>
<td>Rowan</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Total volume (stem wood $>7$ cm diam.) 475 613 544

Coniferous trees 73 279 176
Deciduous trees 402 334 368
Percentage of deciduous trees [%] 84.6 54.5 67.6

2 Site description

The Lägeren research site (CH-Lae in CarboEurope IP) is situated at 47°28’40.8” N; 8°21’55.2” E at 682 m a.s.l. (base of tower) on the south-facing slope of the Lägeren mountain (866 m a.s.l.), approximately 15 km northwest of Zurich, Switzerland. The south slope of the Lägeren mountain marks the boundary of the Swiss Plateau, which is bordered by the Jura and the Alps. This site became a permanent station of the Swiss air quality monitoring network (NABEL) in 1986. First eddy covariance flux measurements were carried out during the winter season 2001/2002 to quantify fog water fluxes and the flux of dissolved inorganic ions therein (Burkard et al., 2003). Routine CO$_2$ and H$_2$O flux measurements as a contribution to the CarboEurope IP network started on 1 April 2004. Flux measurement instruments were installed on a horizontal boom extending from the top of a 49 m tower in south-western direction to yield a measurement height $z=59$ m above local ground.

The natural vegetation cover at the research site is a productive, managed beech forest. The western part is dominated by broad-leaved trees, mainly ash, sycamore and beech whereas in the eastern part beech and spruce are dominating (Table 1). The forest stand has a relatively high diversity concerning species, age, and diameter distribution. We counted 105 to 185 years for spruce and 52 to 155 years for beech. This structure is the result of a consequent intensive management by Swiss Selective Cutting and natural regeneration during the last decades after the transition to the so-called “permanent forest system”. The mean tree height of the dominant trees was 30.6 m, the highest spruces reach 42.2 m. The aerodynamic displacement height $d$ was estimated at 18 m, yielding an effective measurement height $z=Z−d$ of $≈30$ m.

The pronounced linear topography of the Lägeren mountain ridge leads to a very nicely channeled atmospheric flow that is mostly along the slope with two distinct lobes of the flux footprint towards the West (primary maximum occurrence of wind direction) and the East (secondary maximum).

3 Methods

3.1 N$_2$O flux measurements with a quantum cascade laser system

We used a QCLAS (Nelson et al., 2002; Tuzson et al., 2007) in combination with an ultrasonic anemometer (Gill Solent HS, sampling at 20 Hz) used as the standard instrument of the Lägeren CarboEurope IP flux site. In addition to the configuration described in Neftel et al. (2007), who used an earlier version of the same instrument, efforts were made to also quantify water vapor (H$_2$O) with the same laser that measures nitrous oxide (N$_2$O) and carbon dioxide (CO$_2$). The corresponding absorption lines were at 2242.74 cm$^{-1}$, 2242.90 cm$^{-1}$ and 2243.11 cm$^{-1}$ for H$_2$O, $^{13}$CO$_2$ and N$_2$O, respectively. Unfortunately, it is not possible to measure the most abundant CO$_2$ isotopomer simultaneously with N$_2$O and H$_2$O, within the scanning range of a QCL in the 2240 cm$^{-1}$ wavelength region. The commercially available instrument (Aerodyne Research Inc., USA) was optimized to obtain enhanced stability and precision under field conditions. Both the laser and the detector were thermoelectrically cooled, giving a cryogen-free instrument, which can run unattended for extended time periods.

Samples were measured at 65 mbar in a 0.5 L astigmatic multipass absorption cell with a path length of 56 m. At this pressure, the collisional broadening of the absorption lines is sufficiently small to allow the separation of the absorption lines and yield a well defined baseline (Fig. 1). The absorption spectra were fitted numerically based on a set of parameters including line positions, line strengths, broadening coefficients, and lower state energies taken from the HITRAN database (Rothman et al., 2005). Volume mixing ratio values were calculated using the Beer-Lambert law.

The QC laser was driven with short ($≈10$ ns) pulses in a 1% duty cycle at $−31^\circ$C. The signal-to-noise ratio was enhanced by normalizing pulse-to-pulse intensity variations with temporal gating on a single detector. Data acquisition and analysis was done by TDLWintel, a commercially available software package (Nelson et al., 2004). Absorption spectra at 2241 cm$^{-1}$ were recorded by sweeping the laser across the absorption features at a rate of about 5 kHz. Co-
averaged spectra were quantified at 5 Hz. Background (N\textsubscript{2}, 99.999%) and reference (pressurized air) spectra were measured every 30 min. This regular procedure is called autocalibration in the following text.

The calibration procedure consisted of measurements of nitrogen (background) and pressurized air with known concentrations of CO\textsubscript{2} and N\textsubscript{2}O (reference), traceable to a CMDL standard (Climate Monitoring and Diagnostics Laboratory, NOAA, USA). For water, 10-min averages were compared to the values obtained using a Thygam VTP6 (Metelabor, Switzerland) dewpoint mirror. The linear regression of the H\textsubscript{2}O data from the full measurement campaign was forced through zero and gave a calibration factor of 1.09 ($r^2=0.99$). Background and reference were measured for 20 s each after flushing of the measurement cell. The precision was determined every 30 min from the reference measurement, i.e. the calibration measurement was also used to determine precision. This is relevant because changes such as optical alignment, laser intensity and detector sensitivity are very likely to increase the noise level and thus reduce precision. Typical values were 0.3 ppb root-mean-square error (at 1 Hz) for N\textsubscript{2}O and 0.7 ppm root-mean-square error (at 1 Hz) for CO\textsubscript{2}. For water, the corresponding value was about 50 ppm, determined from ambient air during periods with only small concentration changes. Ambient air, nitrogen and reference gas were sampled at 6 L min\textsuperscript{-1}. All three had to pass the same filter to obtain similar pressure conditions in the cell during background, calibration and measurement. The calibration factor for N\textsubscript{2}O and H\textsubscript{2}O showed slight drifts that are probably due to an increasing pressure drop over the filter, which was changed three times during the measurement campaign. Due to filter clogging, the cell pressure varied between 53 and 85 hPa. The most pronounced variations in calibration factor were found for N\textsubscript{2}O. They were always smooth and less than 4% difference was caused by filter changes. Therefore, the calibration procedure was adequate. It would nevertheless be preferable to add a pressure control to the sampling system. This would also allow longer calibration intervals.

The QCLAS was located in an air conditioned room, and samples were drawn at 149 L min\textsuperscript{-1} and $-270$ hPa through 55 m PVC tubing (inner diameter I.D. of 14 mm), the tip of which was attached close to the sonic anemometer. The intake was placed 0.2 m from the sonic anemometer’s sensor head in the horizontal direction such that the air flow has no influence on the vertical wind speed measurements. A smaller Teflon hose (I.D. 4 mm) with a length of $\approx$ 3 meters was then connected to the instrument. This Teflon hose and the QCLAS sample cell were purged with a flow rate of 6 L min\textsuperscript{-1} using an oil-free vacuum pump (Varian Triscroll 300). The full sampling system was kept at turbulent flow conditions and had a time delay of $\approx$ 4 s with a response time (cell volume/flow) of 0.3 s. For the covariance computations the actual delay time for each 30-min averaging period was considered by searching for the maximum cross-correlation around this expected delay. A maximum delay of 5 s (25% longer than expected) was defined for this search.

3.2 N\textsubscript{2}O flux calculations

The eddy covariance flux measurement method (e.g. Baldocchi, 2003; Eugster et al., 1997) is the standard method within CarboEuropeIP and well described by Aubinet et al. (2000) for the standard CO\textsubscript{2} and H\textsubscript{2}O flux measurements that were also carried out at the Lägeren site using a Licor 7500 (Lincoln, Nebraska, USA) non-dispersive open-path infrared gas analyzer (IRGA). For the special purpose to add QCLAS flux measurements, we however had to modify our data acquisition and data processing method as described in the following.

The QCLAS data processing computer handed over the mixing ratio values of N\textsubscript{2}O, CO\textsubscript{2}, and H\textsubscript{2}O at a rate of 5 Hz via a serial RS-232 data connection to the eddy covariance computer. In order not to disturb the covariance computations that are performed at regular 30-min intervals, these autocalibration procedures were scheduled to begin shortly before the half-hour time marks, and end shortly thereafter. Since the sonic anemometer and IRGA data arrived at 20 Hz, whereas the QCLAS data arrived at 5 Hz, the latter had to be replicated 4 times in the raw data set. When processing the raw data files with a further development of the software mentioned in Eugster et al. (1997) that has also undergone the CarboEurope IP software intercomparison (T. Foken, personal communication), we trimmed the 30-minute periods to roughly 29 min periods separated by the missing data blocks during autocalibration. All other procedures, however, corresponded to the standard processing algorithm, except for (a) that a high-frequency damping loss correction as suggested by Eugster and Senn (1995) did not appear to be essential (see Section 4.2), and (b) that the correct application of the Webb et al. (1980) density flux correction had to be evaluated first (see Sect. 5.1).
3.3 Error assessment

A great proportion of our analyses presented in the following sections will assess uncertainties and errors (random and systematic) in our \( \text{N}_2\text{O} \) flux measurements. We will argue that since the eddy covariance approach is based on the general correlation equation we should be able to identify insignificant flux values via statistically insignificant correlation coefficients. The general correlation equation is (Wilks, 2006, p. 51)

\[
r = \frac{w'c'}{\sqrt{w'^2 \cdot c'^2}} ,
\]

where \( r \) is Pearson's correlation coefficient, \( w \) is the measured wind speed component perpendicular to the dynamic streamlines (in \( \text{m s}^{-1} \)), and \( c \) is the concentration measurement. Overbars denote averages over time intervals, and primes denote short-term deviations thereof. The covariance \( w'c' \) is the turbulent flux of the entity, which depending on the type of measurement that \( c \) represents must be scaled accordingly to yield flux density values. For example, the \( \text{HO}_2 \) concentration delivered by the IRGA is in \( \text{mmol m}^{-3} \), thus the \( \text{HO}_2 \) flux obtained from that instrument, directly yields \( \text{mmol m}^{-2} \text{s}^{-1} \). In the case of the QCLAS that measures mixing ratio, the unit of \( c \) is ppb for \( \text{N}_2\text{O} \), which corresponds to \( \text{nmol mol}^{-1} \). The flux of \( \text{N}_2\text{O} \) measured with QCLAS it thus derived from the covariance (which yields \( \text{nmol mol}^{-1} \text{ m s}^{-1} \)) multiplied by \( \rho_a/M_a \), where \( \rho_a \) is the density of air (in \( \text{kg m}^{-3} \)), and \( M_a \) is the molar mass of air (\( \approx 0.028965 \text{ kg mol}^{-1} \)).

Signal-to-noise ratios (SNR) of the QCLAS data for a specific frequency \( f \) were defined as follows (see Eq. A2 in Eugster et al., 2003):

\[
\text{SNR}(f) = \sqrt{\frac{c(f)^2}{\text{(RMS noise)}^2}} - 1 ,
\]

where RMS is the frequency-independent root-mean-square of the white noise level of the instrument (for determination of the white noise level see Section 4.1).

4 QCLAS instrument performance

4.1 \( \text{N}_2\text{O} \) variance spectra

An example spectrum of measured \( \text{N}_2\text{O} \) variance is shown in Fig. 2a. Since we set the instrument to auto-calibrate itself every 30 min, the effective length of continuous data is 29'10" followed by a gap of 50". Thus, we cannot compute 1-hour spectra as is generally done (cf. Kaimal et al., 1972) to see how spectral densities approach zero with lower frequencies. Therefore, in our example we computed the spectral densities for half-hour periods, knowing that the densities at low frequencies are underestimated compared to those expected in uninterrupted hourly time series.

First of all, the spectrum in Fig. 2a shows the effect of oversampling. We collected data at 20 Hz, whereas we set the QCLAS to provide 5 Hz data. Although we could have set the QCLAS to output 20 Hz, this would have reduced the integration time per sample and thus increased the signal-to-noise ratio. Moreover, the volume of our sample cell, the tube length and flow rate suggest that our QCLAS can provide at most 2–3 Hz data. This estimate was determined experimentally, treating the sample cell as a mixed reactor and fitting rapid concentration changes according to

\[
e_{\text{N}_2\text{O}}(t) = c_{\text{N}_2\text{O}}(0) \cdot \exp(-t/\tau) ,
\]

where \( t \) is the time in s and \( \tau \) is the time constant. The time constant of the instrument alone is \( \approx 0.3 \text{ s} \), and increases to \( \approx 0.45 \text{ s} \) for the full sampling setup. This corresponds to a low-pass filter with a cutoff frequency \( f_c = 1/(2\pi \tau) \), which is 0.4 Hz for the full setup. Thus, a 5 Hz sampling rate (for which the Nyquist frequency is 2.5 Hz) seemed adequate. The noise of flux measurements depends on a complicated set of sensor properties such as the instrument’s white noise, pink noise (e.g. drift), and response. These effects and interactions have already been discussed in more detail for a QCLAS by Saleska et al. (2006).

In Fig. 2a all information to the right of the broken vertical line – the Nyquist frequency that separates the resolved from the unresolved frequencies – is related to the oversampling of the QCLAS signal. The true noise level for \( \text{N}_2\text{O} \) is therefore not to be sought at the highest frequencies, but left of the Nyquist frequency. We chose a display in Fig. 2a where white noise is shown as horizontal lines. The transition from the inertial subrange slope indicated by the theoretical \( f^{-5/3} \) decay of spectral density with increasing frequency towards the horizontal can nicely be seen. Thus, we defined the noise level of the QCLAS’s \( \text{N}_2\text{O} \) signal to be the spectral density of the segment showing almost no dependency on frequency. This is a more conservative estimate than just taking the spectral density at the Nyquist frequency.

With reference to this noise level we can see a clear QCLAS signal up to 1 Hz. As expected, the signal disappears at higher frequencies. Nevertheless, Fig. 2a shows that the overall performance of the QCLAS for eddy covariance flux measurements of \( \text{N}_2\text{O} \) should be sufficient, at least for daytime conditions where the high frequencies are not contributing much to the total flux. Based on our definition of the instrument noise level, we can now compute the signal-to-noise ratios of the whole spectrum in Fig. 2a. For the energy containing range of the spectrum – the intermediate frequencies which are most relevant for turbulent mixing and exchange – we get very good ratios of up to 20. The signal-to-noise ratio where the measured spectrum separates from the theoretical inertial subrange slope is found at a ratio of 3. The frequency where the measured spectrum drops below a ratio of 1 is indicated by the vertical arrow at \( f = 0.19 \text{ Hz} \).

Despite the very good signal-to-noise ratios for the energy containing range of the \( \text{N}_2\text{O} \) spectra the instrument noise
contributes almost 50% of the variance signal on the half-hourly averages displayed in Fig. 2a. This is much better seen when an area-preserving variant of the same information is given as in Fig. 2b, where the spectral densities were multiplied with $f$.

4.2 N$_2$O flux cospectra

Figure 3 shows a rather good behavior in the high frequencies. Despite the fact that the QCLAS has a limited time response of 2–3 Hz, there is no need to apply any damping loss correction (Eugster and Senn, 1995). This is not unexpected since the most relevant information for eddy covariance flux measurements is found at much lower time scales than the response rate of the QCLAS. When comparing the cospectra with idealized 1-h cospectral curves by Kaimal et al. (1972) (broken curve in Fig. 3), we see a very good agreement at frequencies >0.005 Hz. The difference at lower frequencies has two main reasons: (1) the autocalibration of the QCLAS at 30-min intervals results in shorter uninterrupted intervals of continuous data that in consequence lead to lower cospectral densities at low frequencies; and (2) the need for detrending the time series for the Fourier transformation (Panofsky and Dutton, 1984, Stull, 1988) further reduces the cospectral densities at lower frequencies. This may lead to conservative estimates of the N$_2$O flux estimates. Given the stability of the instruments we would opt for longer periods (1–2 h) between autocalibration in future studies.

5 Possible sources of error in N$_2$O flux measurements

There are many sources of errors that could potentially influence the eddy covariance measurements. It is unavoidable to screen out a certain fraction of data due to plausibility reasons. This is sometimes termed “quality control” and within CarboEurope IP it was agreed to use a common quality flag system that gives flag 0 for highest quality research grade data points, flag 1 for good quality data that are perfect for long-term budgeting of the fluxes, and flag 2 for all other data points, including missing values due to technical problems, power failures, and more. The concept goes back to that proposed by Foken and Wichura (1996). In practice, two checks are performed to yield the quality flag information: (1) a stationarity test, and (2) a test whether $\sigma_u/u_s$ as a function of the stability parameter $z/L$ (Monin and Obukhov, 1954) conforms with the empirical model suggested by Foken and Wichura (1996). For the first test (stationarity test) one compares the arithmetic mean of six 5-min flux averages with the 30-min covariance. If the deviation from an idealized 1:1 ratio – which could be expected if turbulence is not covering larger time scales than 5 min$^1$ – is $<30\%$, $<100\%$, or $>100\%$ then flags 0, 1, and 2, respectively, are given. This procedure is repeated for the second test, and the larger of

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This assumption could be questioned; the theoretical ratio based on the Kaimal et al. (1972) cospectra for idealized conditions would actually be 0.92; see Eugster et al. (2003).

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Fig. 2. Example spectra of N$_2$O variance from 30.10.2006, 11:00–12:00 CET, (a) in log-log and (b) in log-linear display where spectral densities $S_c(f)$ were multiplied with $f$ to preserve areas below the spectral curve (in bold). Symbols show bandwidth averaged spectral densities of the first and second half hour, respectively, with the bold line the average of both. The expected inertial subrange slope is indicated by the $f^{-5/3}$ line in (a) and the $f^{-2/3}$ in (b), respectively. The vertical broken line shows the Nyquist frequency of the QCLAS data acquisition (2.5 Hz). Thin horizontal (a) or curved lines (b) give the noise level of the instrument and the corresponding levels for signal-to-noise ratios of 1, 5, 10, and 20, respectively. The arrow shows the frequency where the QCLAS signal-to-noise ratio is 1. Mean horizontal wind speed during the period was 0.78 m s$^{-1}$. See text for interpretation.
the two flags is assigned to the respective data point. Still, some questions remain, as was demonstrated by Geissbühler et al. (2000): the uncertainty in this test itself lies mostly in the uncertainty to quantify \( z/L \) outside the neutral stability range, and a huge deviation of \( \sigma_u/u_\ast \) may just indicate that \( z/L \) was wrong.

For our purpose we assessed whether despite such criticism the current quality flagging system of CarboEurope IP could help to identify outliers and bad data points also in \( \text{N}_2\text{O} \) fluxes. But before being able to do so we need to identify questionable data points in a completely independent way. We did this by investigating which fluxes are significant and which ones may be random fluxes. This involves two steps: first we carefully discuss the issue of density flux corrections (Webb et al., 1980) and then we discuss the issue of statistical significance of \( \text{N}_2\text{O} \) fluxes, followed by the comparison with the CarboEurope IP flag system.

5.1 Density Flux Correction

Webb et al. (1980) presented the following equation for the density flux correction of eddy covariance flux measures:

\[
F = \frac{w^2 \rho_c' + \mu \left( \frac{\rho_c}{\rho_a} \right) w^2 \rho_a'}{1 + \mu \sigma \left( \frac{\rho_c}{T} \right) w^2 T},
\]

where \( w \) is vertical wind speed in \( \text{m s}^{-1} \), \( \rho_c, \rho_a, \text{and } \rho_v \) are the densities of gas \( c \), air, and vapor, respectively, in \( \text{kg m}^{-3} \), \( T \) is air temperature in \( \text{K} \), and \( \mu = m_a/m_v \) and \( \sigma = \rho_v/\rho_a, m_a \) and \( m_v \) are the molar masses (“weights”) of dry air and water vapor, respectively, in the units \( \text{kg mol}^{-1} \).

This equation has basically three additive terms: (I) the measured flux (or covariance), (II) a correction for concurrent moisture fluxes, and (III) a correction for concurrent sensible heat fluxes. As stated by Webb et al. (1980) terms II and III can be neglected in an instrument that measures the dry mole fraction. In the scientific community it is generally agreed that term III can be omitted in closed-path systems, while term II must be considered (as we did in our computations) unless the air is dried or moisture is measured and corrected for.

5.2 Significance of fluxes

\( \text{N}_2\text{O} \) flux measurements reported in the literature (see also Table 2) show large scatter and thus it is often difficult to distinguish true peak effluxes from randomly large fluxes. It is thus important to assess which flux values actually were distinguishable from a random outcome. This is not necessarily identical to small fluxes, since significant fluxes result only from significant correlations when measured with the eddy covariance method. This shall be elaborated in more detail in this section. It becomes clear by studying Eq. (1) that it is meaningless to try to define a precise minimum detectable flux for eddy covariance systems as we would do for standard mean concentration measurements. The reason is that both components in the denominator of Eq. (1) are always greater than zero in a turbulent atmosphere, no matter whether there is a flux or not. This aspect will be illustrated in more detail in the following paragraphs.

We can test the significance of Pearson’s correlation coefficient \( r \) using Student’s \( t \) test,

\[
t = r \sqrt{\frac{n - 2}{1 - r^2}},
\]

(DMK/DPK, 1977, p. 93) where \( n \) is the number of samples per record (9000 at 5 Hz operation rate). By rearranging Eq. (5) we get the value for significant correlation,

\[
r = \frac{t_p}{\sqrt{n - 2 + t_p^2}},
\]

using the specified \( p \) value to determine \( t_p \). Figure 4 clearly reveals the effect of insignificant correlation coefficients when compared against the values obtained with Eq. (6). We rejected all fluxes where either \( r \) was insignificant at \( p \leq 0.0001 \) (35.7% of records) or the momentum flux was not directed towards downwards (20.5%).
Table 2. Comparison of eddy covariance \(\text{N}_2\text{O}\) flux measurements over forests with selected results from agricultural ecosystems.

<table>
<thead>
<tr>
<th>Ecosystem &amp; Locality Measure</th>
<th>Chamber Flux (\mu\text{mol m}^{-2}\text{h}^{-1})</th>
<th>Eddy Flux (\mu\text{mol m}^{-2}\text{h}^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Forest ecosystems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed beech &amp; spruce forest; Switzerland, Lägeren</td>
<td></td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>Autumn, 4 weeks, gaps replaced by zero</td>
<td>0.8±0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autumn, 4 weeks, no gap filling</td>
<td>1.9±0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interquartile range, no gap filling</td>
<td>−2.7…5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interquartile range after gapfilling</td>
<td>0.0…0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absolute min…max</td>
<td>−22…83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rain events ((\text{N}_2\text{O}) losses only during ≤6.5 hours)</td>
<td>18.3±8.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Old beech; Denmark, Lille Bøgeskov(^a)</td>
<td></td>
<td></td>
<td>Pihlatie et al. (2005b)</td>
</tr>
<tr>
<td>Spring mean, 5 weeks</td>
<td>0.7±0.1/1.1±0.8</td>
<td>0.4±0.1</td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>0.7/0.6</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0.01…2.1/−0.3…6.7</td>
<td>−0.1…1.5</td>
<td></td>
</tr>
<tr>
<td>Boreal aspen forest; Canada, Saskatchewan</td>
<td></td>
<td></td>
<td>Simpson et al. (1997)</td>
</tr>
<tr>
<td>Full period, summer, 5 months</td>
<td>0.11 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0.16…0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spruce-fir-beech forest; Austria, Tyrol</td>
<td></td>
<td></td>
<td>Kitzler et al. (2006)</td>
</tr>
<tr>
<td>Two years, bi-weekly sampling</td>
<td>0.31 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Agricultural ecosystems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agriculture, fertilized; UK, Scotland, Stirling</td>
<td></td>
<td></td>
<td>Wienhold et al. (1994)</td>
</tr>
<tr>
<td>Range, April</td>
<td>9.8…29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harvested wheat field; Denmark, NW Sealand, August</td>
<td></td>
<td></td>
<td>Wienhold et al. (1995)</td>
</tr>
<tr>
<td>Range</td>
<td>3.3…9.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manured plot; Canada Ontario</td>
<td></td>
<td></td>
<td>Edwards et al. (2003)</td>
</tr>
<tr>
<td>Average</td>
<td>low fluxes</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>Peak after 120 mm rain</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corn field after fertilization; Canada, Ottawa</td>
<td></td>
<td></td>
<td>Pattey et al. (2006)</td>
</tr>
<tr>
<td>Baseline period</td>
<td>&lt;2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After fertilization, 67 mm rain</td>
<td>8.2…14.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak emissions</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 days after fertilization</td>
<td>7…15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final week</td>
<td>2.9…6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maize fields, irrigated and fertilized; France, Landes de Gascogne</td>
<td></td>
<td></td>
<td>Laville et al. (1999)</td>
</tr>
<tr>
<td>Range</td>
<td>6.4…71</td>
<td>5.1…103</td>
<td></td>
</tr>
<tr>
<td>Grassland, intensively grazed and fertilized; Ireland, Cork</td>
<td></td>
<td></td>
<td>Scanlon and Kiely (2003)</td>
</tr>
<tr>
<td>Background below</td>
<td>&lt;7.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean over 8 months</td>
<td>≈5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak emissions (3 events)</td>
<td>≈130…250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grassland, fertilized; Switzerland, Oensingen</td>
<td></td>
<td></td>
<td>Neftel et al. (2007)</td>
</tr>
<tr>
<td>Background range</td>
<td>&lt;8.2</td>
<td>−43.3…4.1</td>
<td></td>
</tr>
<tr>
<td>Uptake events</td>
<td>≥−7.4</td>
<td>1.1±0.3</td>
<td></td>
</tr>
<tr>
<td>Intercomparison, August</td>
<td>−0.5±0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Eddy covariance flux measurements were performed in the trunk space of the canopy, not above the canopy; both automatic and manual chamber measurements are given, separated by a slash.

6 Results

The rigorous screening of insignificant \(\text{N}_2\text{O}\) fluxes left us with 44% accepted 30-min flux averages (Figs. 5–6). The rejected fluxes were rather randomly distributed over the whole time series, not indicative of any persistent systematic error that would leave gaps of several hours. Although there are no independent \(\text{N}_2\text{O}\) flux measurement available for validation, there is a possibility to compare \(\text{H}_2\text{O}\) fluxes from the QCLAS system against the standard IRGA flux measurements performed at 20 Hz.

In Fig. 7 the median diurnal cycles of the \(\text{H}_2\text{O}\) flux from both instruments are compared. Since the open-path IRGA system suffers reduced or bad data quality during rain and
dense fog events, we had to further reduce the data set for such a comparison, screening out all periods where the IRGA reported above normal window dirtiness values (a housekeeping variable of the Licor 7500 indicating the current status of the open optical path).

The median diurnal cycles agree quite well with an evapotranspiration peak around 13 h. The pair-wise comparison of H2O fluxes (Fig. 8) also shows a good correlation (adjusted $r^2=0.816$) between open-path IRGA and closed-path QCLAS, however with roughly 13% higher fluxes measured with the open-path than the closed-path system. This relative difference similar to what is typically found when two separate eddy covariance systems with similar instruments are compared (see e.g. Eugster et al., 1997). If such a comparison reveals the system inherent properties of the QCLAS system also for N2O fluxes then we can assume that the N2O flux must be rather accurate.

6.1 The Influence of Rain and Fog on N2O Fluxes

Since we do not yet have sufficient knowledge to develop an elaborate gap filling algorithm similar to the one used for energy and CO2 flux series (see Falge et al., 2001), we chose a conservative approach and replaced all missing or rejected values by zero. This was chosen based on the statistics of the rejected fluxes (see Fig. 6) with a mean ($\pm$ standard error) of 0.23 ($\pm 1.09$) nmol m$^{-2}$ s$^{-1}$. This allowed us to compute a cumulative curve (Fig. 9), which reflects the influence of moisturizing events more clearly than with the 30-min fluxes alone, but it does not automatically imply that each individual flux value that was rejected based on insignificant correlation is automatically a very small flux very close to zero in reality.

Downward fluxes of N2O were not objectively identified as erroneous or insignificant, but the cumulative curve in Fig. 9 clearly shows that there is a much stronger effect of effluxes from the ecosystem towards the atmosphere. Against our expectations that mostly soil processes and thus precipitation events would influence the overall magnitude of N2O effluxes from this unfertilized forest, we did not find a strong correlation between precipitation amount and flux sum over an event. Some precipitation events, although with very little precipitation amounts, showed a very clear response in the N2O flux time series, whereas especially the strong event on 22–23 October did not translate to similarly strong N2O fluxes.

During the same time another research project had a field test running with a PWD-11 visibility sensor from Vaisala OY (Finland) to quantify fog (see Nylander et al., 1997 for technical details). Because the sensor was unmounted in the end of October, visibility information is only available until 25 October. When we compared N2O fluxes also with fog
densities (represented by horizontal visibilities, see Fig. 9, top panel), we found strong indication that especially between 15 and 22 October, when only traces of precipitation were measured, the N₂O fluxes tended to respond to dense fog if it persisted over several hours (Fig. 10). From earlier measurements carried out by Burkard et al. (2003) and Bützerberger (2002) we know that dense and persistent fog at the Lägeren site does not normally produce significant throughfall, but it wettens the forest canopy. This, however does not change soil moisture since no throughfall occurs (data not shown). Thus, a response seen in N₂O fluxes cannot exclusively be related to changes in soil moisture conditions as one would expect. This hypothesis also holds for precipitation events as can be seen in Fig. 11. Cumulative

**Fig. 8.** Pairwise comparison of concurrent H₂O flux measurements obtained from an open-path IRGA and the closed-path QCLAS using the same wind vector data. Each point represents a pair of 30-min average fluxes.

**Fig. 7.** Comparison of concurrent H₂O flux measurements obtained from an open-path IRGA (left; Licor 7500) and the closed-path QCLAS (right) using the same wind vector data. Bold lines and gray shaded areas show the median and interquartile range of the diurnal cycles. Data were lumped into 1-h bins for this comparison.

**Fig. 9.** N₂O fluxes during a 4-week period in autumn 2005 (middle panel; thin bars: 30-minute averages; bold line: cumulative fluxes) measured over a beech-dominated mixed forest at the Lägeren, Switzerland, flux site. The top and bottom panels show the fog and rainfall conditions, respectively. Horizontal visibilities <1000 m are defined as fog (Glickman, 2000). The horizontal gray bars indicate the periods with no fog, light, medium, or dense fog. The crossed circle in the precipitation time series indicates a missing value that was generated by the plausibility check algorithm used by the data owners and indicates that although this precipitation value was screened out, this might have been a relevant event for N₂O fluxes.
Our results suggest a clear increase in net ecosystem N\textsubscript{2}O effluxes during a relatively short period around the beginning of a precipitation event only, but no clear relationship with total rainfall. Our best estimate for N\textsubscript{2}O losses during a typical precipitation event is thus 120 µmol m\textsuperscript{-2} (6.5 h at 18.3 µmol m\textsuperscript{-2} h\textsuperscript{-1}; see Table 2). Short events in a row do not have the same effect on N\textsubscript{2}O fluxes as do events after a clear dry period (Fig. 9). Based on the short duration of our N\textsubscript{2}O flux measurements it is however not yet possible to quantify how this flux relates to the annual CO\textsubscript{2} uptake of −342 g C m\textsuperscript{-2} yr\textsuperscript{-1} determined from November 2004 to October 2005 using an air threshold of 0.95 m s\textsuperscript{-1} to correct for underestimation of nocturnal CO\textsubscript{2} effluxes as measured with our eddy covariance system.

It was argued by Anonymous (2007) that the significance-of-correlation method should remove fluxes around zero, and thus a method based on standard errors of the fluxes would be more appropriate. In fact, the range given by the mean and standard error of the rejected fluxes (see Sect. 6.1) includes zero and thus does not invalidate our approach. The important conceptual difference, however, between our significance-of-correlation approach (SoC) and an approach based on standard error of fluxes (SEF) are the following: SoC does not make an implicit assumption on the statistical distribution of the fluxes that need to be filtered out and should thus be robust even in cases where such outliers show a systematic behavior where the mean of all removed fluxes does not automatically converge to zero. The SEF in contrast implicitly assumes that the measured fluxes have already been screened in an other way and that it can be assumed that no other sources of error other than normally distributed random noise influences the flux values. Thus, as long as the implicit assumptions that are made are correct, then SoC results should not differ significantly from SEF results, whereas for cases where additional errors besides purely clean random noise plays a role we would argue that the SoC method will lead to better results.
There are only very few ecosystem-scale eddy covariance 
\( \text{N}_2\text{O} \) flux measurements over forest available (Table 2) with 
which our fluxes could be compared. The measurements 
carried out in an old beech forest in Denmark (Pihlatie et al., 
2005b) shows trunk-space eddy covariance flux measure-
ments during spring. The duration of their measurements is 
similar to ours (5 vs. 4 weeks) and their average fluxes were 
in the same order of magnitude as ours. The factor two differ-
ence may be a result of above-canopy (our study) vs. below-
canopy measurements, different soil properties and microbial 
activities (autumn has warmer soils than spring), or phenol-
ogy as we noted above. The Pihlatie et al. (2005b) study also 
shows a very convincing comparison of eddy covariance flux 
measurements with automatic and manual chamber measure-
ments (Table 2). Their chamber fluxes are roughly a factor 
two larger than their eddy covariance fluxes. Kitzler et al. 
(2006) measured bi-weekly during two years with manual 
chambers in a similar forest with comparable nitrogen depo-
sition rates (see Burkard et al., 2003 for conditions at our site) 
and yielded mean \( \text{N}_2\text{O} \) fluxes of 0.31±0.02 \( \mu \text{mol m}^{-2} \text{h}^{-1} \). 
Although vegetation, soil type and calcareous ground are 
very comparable to the Lägeren site, their measurements 
were at a higher elevation where trees are less tall and an-
nual temperature is 1.7°C colder (6.5 vs. 8.2°C) which may 
already be responsible for the differences in fluxes. Differ-
ences are larger in the comparison with the fluxes measured 
over boreal aspen forest (Simpson et al., 1997) which shows 
fluxes that are almost an order of magnitude smaller. This 
might again be an indication of the colder climate leading to 
lower \( \text{N}_2\text{O} \) fluxes.

In comparison with agricultural ecosystems (Table 2) the 
\( \text{N}_2\text{O} \) fluxes from our mixed deciduous forest during rain 
events are very similar to those from agricultural fields after 
fertilization. This was not expected and should receive more 
attention in future studies. Furthermore, there is a need to 
increase our understanding of \( \text{N}_2\text{O} \) uptake reported in many 
studies (Pihlatie et al., 2005b, Leahy and Kiely, 2006, Kitz-
ler et al., 2006, Neftel et al., 2007) which is also evident in 
our data (Table 2) in order not to overestimate the greenhouse 
forcing effect of \( \text{N}_2\text{O} \) fluxes from natural ecosystems.

Our speculation that the degradation of senescent leaves of 
deciduous trees at that time of year may be the most im-
portant source of \( \text{N}_2\text{O} \) needs further investigation. We were 
only able to find four other publications that emphasize the 
role of \( \text{N}_2\text{O} \) emissions from plants (Chang et al., 1998, Rusch 
and Rennenberg, 1998, Smart and Bloom, 2001, and Pihlatie 
et al., 2005a). Chang et al. (1998) postulated that signifi-
cant amounts of \( \text{N}_2\text{O} \) may also be emitted via herbaceous 
plant transpiration, but also found that watering the soil with 
an \( \text{N}_2\text{O} \) rich solution immediately increases \( \text{N}_2\text{O} \) emissions 
from the above-ground parts of the plant, which suggests that 
\( \text{N}_2\text{O} \) is conveyed to the leaves via the transpiration stream. 
Thus the primary process responsible for producing \( \text{N}_2\text{O} \) is 
necessarily to be found in the above-ground components 
of plants. Rusch and Rennenberg (1998) found similar con-

ditions in trees. Smart and Bloom (2001) used \( ^{15} \text{N} \) labeled 
fertilizer to be able to more specifically find out where plant 
emitted \( \text{N}_2\text{O} \) is actually produced. In contrast to the previous 
two studies they found that labeled \( \text{NH}_4^+ \) fertilizer did not 
increase \( \text{N}_2\text{O} \) emission significantly, whereas \( \text{NO}_3^- \) fertilizer 
did. Leaf \( \text{N}_2\text{O} \) emissions were correlated with leaf nitrate 
asimilation activity, and measured isotopic signatures sup-
ported their interpretation that direct \( \text{N}_2\text{O} \) production by 
plant \( \text{NO}_3^- \) assimilation must be responsible for these \( \text{N}_2\text{O} \) 
emissions, and not \( \text{N}_2\text{O} \) produced by microorganisms on root 
surfaces which is then conveyed to the leaf surface via the 
transpiration stream. Finally, Pihlatie et al. (2005a) also used 
\( ^{15} \text{N} \) labeled fertilizer with beech seedlings. Their interpreta-

tion allows for several processes that could lead to \( \text{N}_2\text{O} \) emis-
sions from the leaves and shoot, such as transpiration, \( \text{N}_2\text{O} \) 
formation in the leaves and \( \text{N}_2\text{O} \) diffusion through the bark. 
The conditions at our site are further complicated by the fact 
that fog also tends to be rich in \( \text{NO}_3^- \) (Burkard et al., 2003), 
such that fog may directly provide this source of nitrogen to 
leaves and micro-organisms living on and in leaves. At 
the same time, the wet environment on the leaves during events 
with dense fog could stimulate the denitrification process on 
and in the leaves, even if leaves are not senescent. Still, one 
might expect higher rates of \( \text{N}_2\text{O} \) emissions during the sce-
nescence of leaves when the two nitrogen sources from the 
fog water deposited to the leaves and from the nitrogen in the 
leaves are combined.

8 Conclusions

Net \( \text{N}_2\text{O} \) efflux from a deciduous tree dominated mixed 
forest in Switzerland averaged 0.8±0.4 \( \mu \text{mol m}^{-2} \text{h}^{-1} \). Al-
though these values are in the range reported by others (Ta-
ble 2), these fluxes are relatively small and difficult to mea-
sure with currently available technology. Thus, a rigorous 
screening of data obtained from our Quantum Cascade Laser 
Absorption Spectrometer was necessary. Since we used 
the eddy covariance method for flux measurements we ar-
gued that the significance-of-correlation approach that uses 
the maximum cross-correlation value between vertical wind 
speed component and concentration fluctuations is a good 
statistical approach to separate significant fluxes from in-
significant fluxes, which are a combination of very small 
fluxes ("below detection limit" given that such a detection 
limit is valid for eddy covariance flux measurements) and 
those fluxes, where the statistics that can be retrieved from 
the time series do not support the alternative hypothesis that 
the flux differs significantly from zero, even if the absolute 
value appears to be large.

To the best of our knowledge this was the first attempt to 
simultaneously determine \( \text{N}_2\text{O} \), \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) with a single 
QC laser. However, the scanning range of the QCL limits the 
 simultaneous spectroscopic quantification to \( ^{13} \text{CO}_2 \). There-
fore, only \( \text{H}_2\text{O} \) measurements were used for cross-validation

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with an independent, well established analyzer. The agreement of H2O concentrations and fluxes with a standard Licor 7500 open-path IRGA was very encouraging and supports the idea that future developments should include this additional H2O measurement to compute true dry-mole fractions for N2O that would eliminate the need to apply a Webb et al. (1980) moisture density flux correction. We however showed that this correction is only small and it is not expected to have a large influence on our interpretation of eddy covariance N2O fluxes measured with QCLAS.

A longer period would have been necessary to substantiate the greenhouse gas flux via N2O in relation to the annual net CO2 uptake of −342 g C m−2 yr−1 of this forest ecosystem in terms of carbon dioxide equivalents. A more detailed assessment of the forestry management practices, especially the estimation of wood harvests and the C export via this pathway would certainly increase the relative importance of N2O fluxes in future assessments and should be continued beyond the time frame of the CarboEuropeIP project. Besides the expected outcome that N2O fluxes respond to precipitation events we hypothesized that canopy wetting by fog and drizzle must also be a relevant, yet unexplored process leading to N2O emissions from above-ground biomass, probably from senescent leaves. In future studies it would be desirable to cover longer periods and assess the effect of phenology in deciduous tree dominated forests in more detail.

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