

Comparing laser-based open- and closed-path gas analyzers to measure methane fluxes using the eddy covariance method

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ABSTRACT

Closed- and open-path methane gas analyzers are used in eddy covariance systems to compare three potential methane emitting ecosystems in the Sacramento-San Joaquin Delta (CA, USA): a rice field, a peatland pasture and a restored wetland. The study points out similarities and differences of the systems in field experiments and data processing. The closed-path system, despite a less intrusive placement with the sonic anemometer, required more care and power. In contrast, the open-path system appears more versatile for a remote and unattended experimental site. Overall, the two systems have comparable minimum detectable limits, but synchronization between wind speed and methane data, air density corrections and spectral losses have different impacts on the computed flux covariances. For the closed-path analyzer, air density effects are less important, but the synchronization and spectral losses may represent a problem when fluxes are small or when an undersized pump is used. For the open-path analyzer air density corrections are greater, due to spectroscopy effects and the classic Webb–Pearman–Leuning correction. Comparison between the 30-min fluxes reveals good agreement in terms of magnitudes between open-path and closed-path flux systems. However, the scatter is large, as consequence of the intensive data processing which both systems require.

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1. Introduction

Recent increase of atmospheric methane concentration has raised the attention of the scientific community around this potent greenhouse gas, a global warming potential 21 times greater than carbon dioxide on a 100-year horizon (Bridges and Batjes, 1996; Lelieveld, 2006). The large uncertainty of an individual source and sink and their temporal variability (Bousquet et al., 2006; Solomon et al., 2009) require systematic observations of the fluxes over extended time periods with direct methods such as static or dynamic chambers and eddy covariance (Lai, 2009).

The eddy-covariance method has emerged in the last few decades as a leader for observing energy and gas exchanges, in particular water vapour and carbon dioxide, above natural or managed ecosystems (Baldocchi et al., 2001). Some of the advantages of using this technique, compared to other methods, are that the measurements are non-intrusive and quasi-continuous and its spatial representativeness is comparable to the ecosystem scale. Furthermore, the method is direct, in the sense that the net flux across land–vegetation–air interface is measured without using

any parameterization (such as diffusivity coefficients, allometric relationships, physiological functions).

The eddy covariance method assumes that fluxes originate from statistically homogeneous surfaces and can resolve many scales of temporal variability (Katul et al., 2001). Short and continuous integration intervals (e.g., half-hourly), often achievable only with automated methods, are necessary to capture all the temporal variability contained in biophysical processes and the linkage with their drivers. Quasi-continuous sampling and intelligent gap filling are able to produce integrated daily, seasonal and annual budgets.

The recent advances in laser spectroscopy give researchers the ability to measure radiative greenhouse gases, such as methane, nitrous oxide, carbon dioxide and isotopes of water vapour and carbon dioxide (Baer et al., 2002; Gharavi and Buckley, 2005) at fast sampling rates of 10–20 Hz and resolution adequate for the application of eddy covariance. These gas analyzers are divided into two main categories: closed- and open-path analyzers. The main difference between the two types of analyzers is that the air sampling location and the optical cell are coincident for an open-path and separated for a closed-path. This difference is not just a formal aspect, but leads to a series of implications in the experimental design and data processing (Haslwanter et al., 2009). For example, a closed-path system requires the use of a power-hungry pump to draw the air through the sampling tube into the optical

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cell. The pump size is based on the volume and operating pressure of the cell, which needs to be flushed at a frequency determined by the cospectra to avoid excessive and undesirable loss of signal. For large sampling cells, solar panels or other small scale energy sources may not be sufficient to supply the power requirements of the pump. In this case, one may need to rely on commercial power lines, limiting the choice of the experimental site. The use of fuel consuming power generators is a possibility, but poses a risk of contaminating the CO₂ and CH₄ measurements; this situation is especially plausible during nights, under calm and variable wind conditions. Alternatively, an undersize pump can be adopted with the inevitable effect of high frequency spectral losses (Horst, 1997), which needs to be corrected using cospectral similarity for that specific site and set-up (e.g., Detto et al., 2010).

The open-path analyzers, though generally having low power consumptions, are not exempt from complications. The instrument body may create distortion in the turbulent flows and is positioned at a distance from the sonic anemometer, sometimes causing small non-negligible spectral losses, in addition to those originating from the path volume averaging (Massman, 2000; Moore, 1986). Air density fluctuations and spectroscopic effects (e.g., line broadening) from changes in temperature, pressure, and water vapour, can be quite large for an open path analyzer and need to be corrected from the total flux calculation (Detto and Katul, 2007; Webb et al., 1980).

The performance of the closed-path system for eddy covariance measurements of methane have been explored for relatively few and short experiments (e.g., Hendriks et al., 2008; Kroon et al., 2010; Rinne et al., 2007; Shurpali and Verma, 1998). In particular, some doubts remain about the applicability of the system for very low fluxes and the corrections needed for air density fluctuations, spectral attenuation, time lags, and phase shifts (Kroon et al., 2007). The recent development of a new open-path methane analyzer gives us the unique opportunity to test and compare the two types of instruments over a range of methane producing landscapes.

This study takes advantage of a network of eddy covariance towers installed from 2007 to 2010 in the western region of the Sacramento-San Joaquin Delta, CA, USA (hereafter the Delta). The soil of the Delta was formed by accretion of organic and mineral material for approximately 7000 years and concomitantly to the rise in ocean levels (Drexler et al., 2009). The surface peat layer has been greatly degraded as a consequence of intensive drainage of the past two centuries (Deverel and Rojstaczer, 1996), but the remaining peat has high organic matter content (Drexler et al., 2009) and in some areas, water tables are shallow, thus potentially favouring anaerobic bacterial processes such as methanogenesis (Conrad, 1989).

In the effort of helping researchers in the area of gas exchanges to better design their experiments, we conducted a series of long and short term observations over several different potential areas of methane emissions: a paddy rice field, a degraded peatland pasture with grazing and methane emitting cows, and a restored wetland dominated by tules (*Schoenoplectus acutus*) and cattails (*Typha latifolia*). In each of the experiments, a closed-path analyzer using cavity ring-down spectrometers (FMA, Los Gatos Research, Mountain View, CA USA) was compared with an open-path analyzer using a wavelength modulation spectroscopy (LI-7700, LI-COR Biogeochemical Sciences, Lincoln, NE, USA).

This study aims to provide advances in understanding the performance and the limitations of eddy covariance method applied to methane, from an instrumental and flux processing point of view. The experimental sites, regardless of fulfilment of the theoretical constraints of planar homogeneity and stationarity, cover a wide range of flux magnitudes and environmental conditions, including dry and flooded surfaces. The sites show different partitioning of net radiation into sensible and latent heat flux, providing an opportunity to examine the changes from air density adjustments in the

Webb–Pearman–Leuning equation (Webb et al., 1980). In addition, the presence of methane-emitting cattle, in the degraded peatland, made it possible to record fluxes up to 1000 nmol m⁻² s⁻¹ when they congregated near the flux tower, permitting us to estimate the lag times and spectral responses with good precision.

2. Method

2.1. Instrumental set-up

The basic eddy covariance instrumentation included a 3D sonic anemometer (Windmaster Pro, Gill Instruments, Lymington Hampshire, UK, at the peatland-pasture and the rice field and a CSAT-3, Campbell Scientific, Logan, UT, USA, at the restored wetland), an open-path CO₂/H₂O infrared gas analyzer (LI-7500, LI-COR Biogeochemical Sciences, Lincoln, NE, USA) and a closed-path fast methane sensor (FMA, Los Gatos Research, CA, USA). FMA uses an off-axis integrated-cavity-output spectroscopy (Baer et al., 2002). At the rice field and restored wetland, the Los Gatos analyzer was equipped with two additional channels for CO₂ and H₂O (fast greenhouse gas analyzer, FGGA). An open-path methane analyzer (LI-7700, LI-COR Biogeochemical Sciences, Lincoln, NE, USA) was installed in conjunction to the permanent closed-path methane analyzer for 3–6 weeks at each site for a total of 4 months (May–August, 2010). The LI-7700 is based on wavelength modulation spectroscopy, yielding a 5 ppb resolution at 10 Hz. It uses a 0.5 m physical path with 60 reflections for a total path of 30 m. It has a nominal power consumption of 8 W.

For the closed-path methane analyzers, two pumps were adopted with different flow rates and power consumption to draw the sampling air through a 4 m tube (inner diameter 6.4 mm made of fluorinated ethylene propylene to minimize sorption/desorption) into the measuring cell (408 cm³) at the operating pressure of approximately 19 kPa. At the peatland-pasture, a scroll pump (BOC ESDP 30A, Edwards, Tewksbury, MA, USA) was used, requiring 770 W of power and capable of producing flow rates near 500 lpm (liter per min) at atmospheric pressure. However, when connected to the small diameter tubing of the LGR analyzer and at a pressure of 19 kPa, the flow rates dropped to about 40 lpm. At the other two sites, a diaphragm pump (N940.5APE-B, KNF Neuberger, Trenton, NJ, USA) was used to reduce the power consumption. The diaphragm pump requires 240 W and is capable of flow rates of 50 lpm, but when connected to the LGR analyzer its flow rate was about 12 lpm.

All instruments were deployed on a tower approximately 3 m above the ground. Additional measurements of temperature and relative humidity were made with a shelter and aspirated HMP-45C sensor (Vaisala Helsinki, Finland). Atmospheric pressure was also measured using Vaisala PTB110. A collection of photographs of the instrumental system is presented in Fig. 1.

2.2. Site description: Sherman Island

Sherman Island is located in the western portion of the Sacramento-San Joaquin Delta at the confluence of the Sacramento and San Joaquin rivers. Like most islands found in the Delta, the land is predominantly flat, below sea level, and primarily used for agricultural purposes since its reclamation in the late nineteenth century through the construction of levees and a network of drainage channels to maintain ground water table below crop root zone.

Due to its geographic location, both, synoptic and regional weather patterns create strong winds between the coast and the interior valley through the Carquinez strait, making it ideal for eddy covariance studies. The experiment commenced in April 2007 and

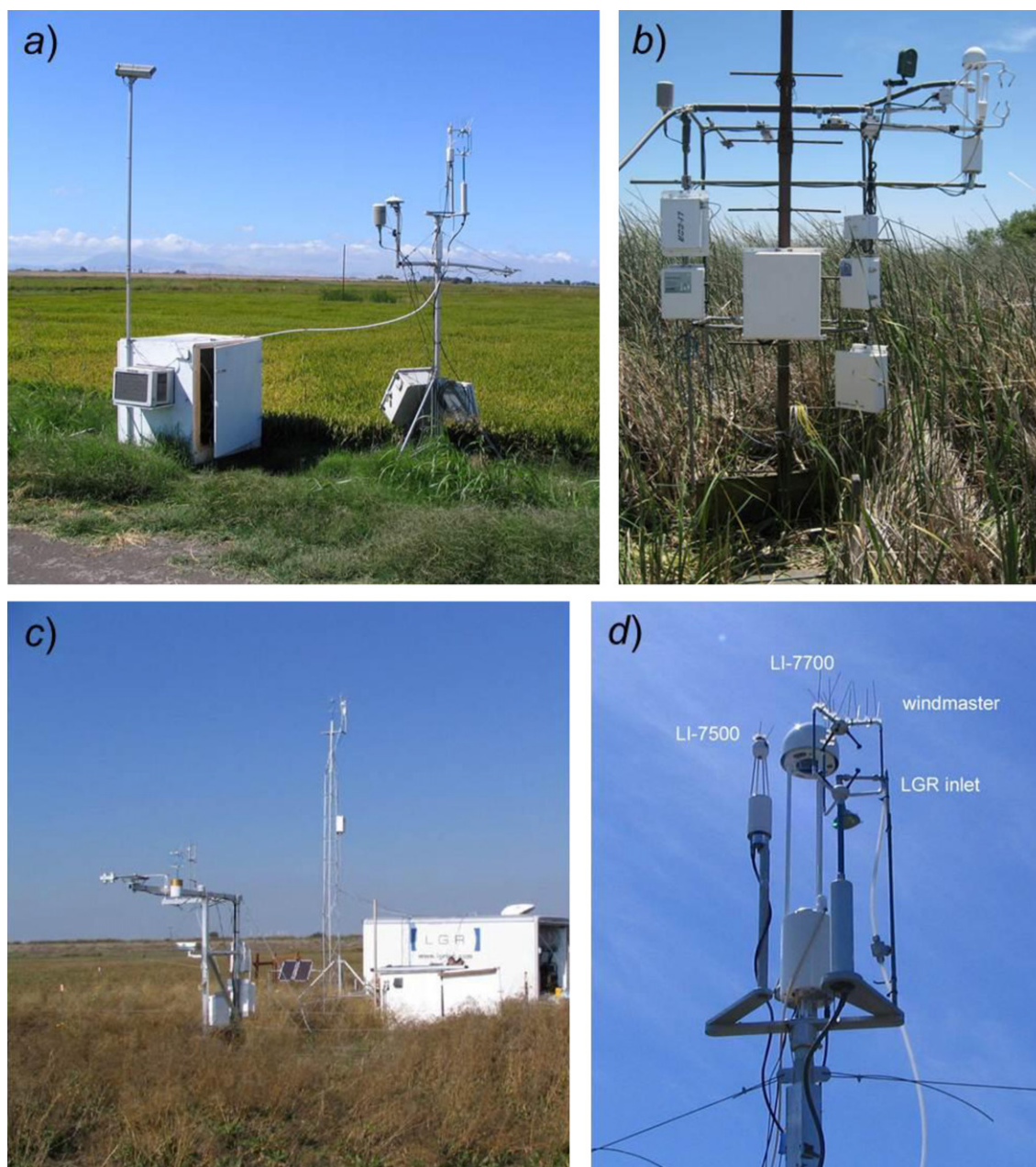


Fig. 1. A collection of photographs of the instrumental set-up: rice paddy field at Twitchell Island (a), restored wetland at Twitchell Island (b), and over the peatland pasture on Sherman Island (c). In panel (d) a detail of the sensors positioning.

the data in the present study include measurements conducted up to August 2010. In 2010, the LI-7700 was added to the site on two occasions, DOY 148–167 and 189–209.

The soil is composed by a layer of oxidized peat (20–40 cm) above a deep peat horizon which extends up to 7 m (Drexler et al., 2009). The site contains an invasive species, perennial pepper weed (*Lepidium latifolium* L.), that is growing quite uniformly in the immediate fetch of the eddy covariance tower (Sonnentag et al., 2011). This weed appears in early March, when new shoots emerged from root buds and persist until the end of October. During the study period, the ground water table fluctuated between 30 and 70 cm below the soil surface. The shallowest water table occurs during the rainy season from December through February. The field is used for cattle grazing. Despite the soil having a modest methane source or sometimes a small sink, mean vertical fluxes can reach $1000 \text{ nmol m}^{-2} \text{ s}^{-1}$ when cows are in the proximity of the tower (see Fig. 2).

2.3. Site description: Twitchell Island

Twitchell Island is located about 10 km northeast of Sherman Island. Twitchell Island has similar soil type as Sherman Island and experiences the same strong westerly winds. There are two experiment sites on the island: a rice field and a restored wetland. These two land management experiments are part of an overall project to reverse subsidence caused by massive peat loss after land reclamation.

At the rice site, an eddy covariance system to measure carbon dioxide and water vapour, identical to the one on Sherman Island, was installed at the beginning of April 2009. During the month of June, the field was flooded and a closed-path FGGA began measuring the methane fluxes. Commercial AC power was not available at the Twitchell Island site. A diesel generator provided the power to run the eddy covariance equipment and was located approximately 70 m south of the tower. The predominant wind direction

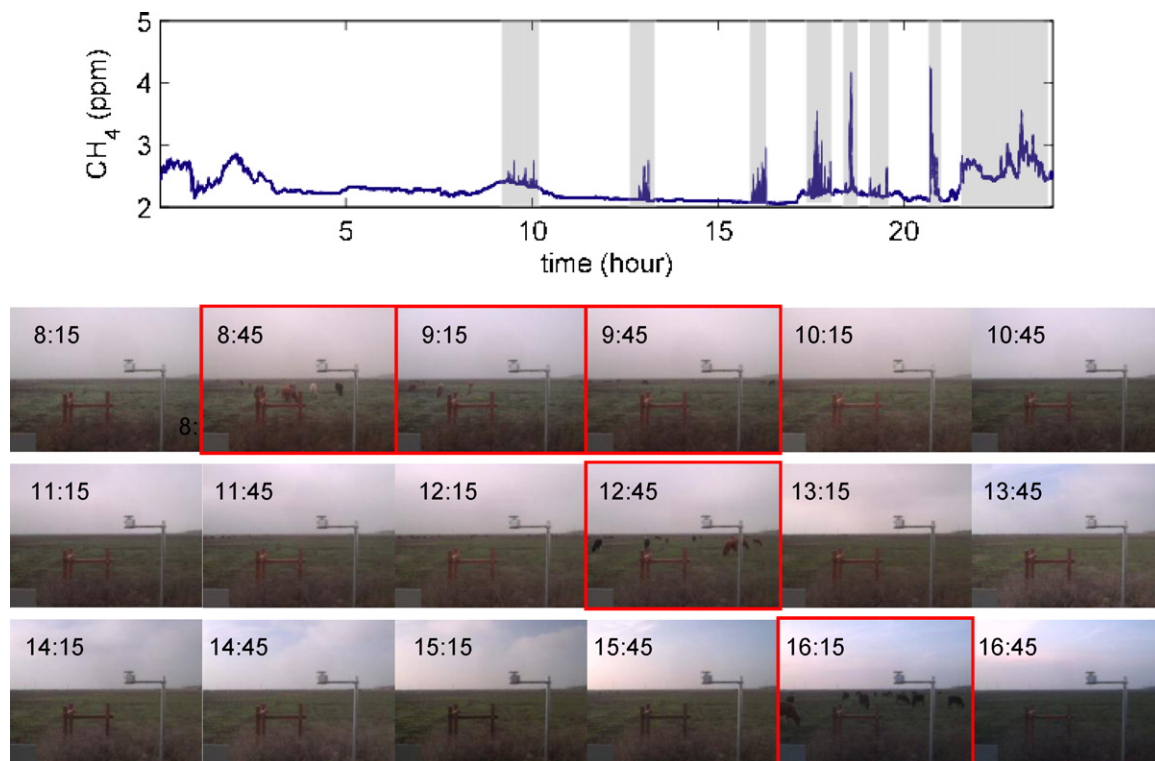


Fig. 2. (a) A 1-day time series of raw methane mixing ratios measured at the height of 3 m on January 5, 2010 by the LGR methane analyzer at Sherman Island site. Grey-shaded areas indicate periods when concentrations were affected by cows' emissions. (b) A photo sequence acquired the same day. The red border indicates periods when cows were present in the field of view of the camera facing west in the direction of the footprint, producing high CH_4 concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is from the west, pushing the diesel exhaust plume away from the tower, however, especially during winter, winds are calmer and wind direction is variable. In 2010, the LI-7700 was installed on two occasions at the rice field site: DOY 125–140, before the field was flooded, and 229–251, during rice cultivation.

The restored wetland is approximately 0.5 km to the east of the Twitchell Island rice site. Construction began in 1997 on 5 ha of wetlands by flooding agricultural land and planting common tules (*S. acutus*). The wetland is split in two parts subjected to different water management treatments. One part is permanently flooded to a depth of 55 cm (i.e. East pond) and the other to a depth of 25 cm (i.e. West pond). Additional site description and previous studies can be found at Miller et al. (2008). An eddy covariance tower was set up in the middle of the East pond, with flux measurements of carbon dioxide and water vapour beginning February, 2010. The LGR fast greenhouse gas analyzer was added in the middle of May. The station is powered by a small diesel generator located about 30 m to the south. The LI-7700 open path methane analyzer was installed on DOY 168 and removed on DOY 189.

2.4. Field calibration

Field calibrations were performed on a regular interval (weekly to bi-weekly) as standard routine of site maintenance using a primary standard gas that is traceable to the NOAA ESRL laboratory in Boulder Colorado (Kitzis and Zhao, 1999). The bottle was connected directly to the inlet tube for the closed-path while an enclosure was used for the open-path. Concentrations before and after calibration were logged.

Lab tests with a standard calibration gas produced 10 Hz concentration measurements with a precision of ± 4 ppb and ± 3 ppb (respectively for the LGR and LI-7700) out of a background of 1900 ppb at ambient temperature of 25 °C. Field records for the LGR

sensors indicate very small instrumental drifts, $1.5(\pm 2)$ ppb/day which can be considered negligible for eddy covariance applications.

2.5. Data sets and spike removal

All the instruments were sampled at a frequency of 10 Hz, allowing for a 5 Hz cospectral cut-off, which is adequate for eddy covariance measurements at these locations (Detto et al., 2010). The raw, 10 Hz data was then divided into daily blocks, resulting in files containing 864,000 data points (from midnight to midnight) per variable (see Fig. 2 as an example). The first data filter included an algorithm developed to detect and remove spikes (values greater than six standard deviations in a 1-min window), bad readings exceeding a reasonable physical range or low diagnostic instrument values (usually during rain and fog).

The fluxes and other statistics were calculated on a 30-min window, but for specific analyses, sub-segments of variable length (from few minutes to few hours) were extracted by visual inspection and their statistics analyzed separately. For each block a coordinate rotation was employed to align the x-axis of the sonic anemometer into the mean wind direction by setting the mean lateral and vertical velocities of each run to zero. Hereafter, vertical wind velocity, air temperature, water vapour, carbon dioxide and methane are abbreviated as w , T , q , c and m , respectively.

2.6. Time lags and phase shifts

Although all the signals were acquired simultaneously, they needed to be synchronized due to the different speeds of digital signal processing among the different instruments, sensor separation and air travelling time in the tube for a closed-path system. Some of these factors may vary between averaging blocks as a function of

wind speed and direction and pump flow rate. Using a maximum cross-correlation method relative to the vertical velocity or temperature, a time lag was determined. However, a residual phase shift may be still present as consequence of first-order response of the instrument (see below). Consequently, it may be more accurate to study the total phase shift $\phi(f)$, as a function of frequency (e.g., Shaw et al., 1998):

$$\phi(f) = \tan^{-1}(2\pi f\tau_c) - 2\pi f\Delta t \quad (1)$$

where the time lag Δt and the first-order time constant τ_c can be evaluated by standard fitting procedure.

For measuring methane, these methods (maximum cross-correlation and total phase) may prove difficult to apply systematically because for small fluxes the signal contains a large amount of noise, which in turn tends to mask the energy at turbulent scales (Detto et al., 2010). As a consequence, (co)spectra and (cross) correlation functions may be distorted from expected shapes. When it was not possible to find an unambiguous peak in the cross-correlation, we used the last value of the lag which has been estimated with less uncertainty.

2.7. Air density effects

The open- and closed-path gas analyzers differ in construction and principle of measurement. The measured tracers, expressed in molar density (ρ_c , mol m⁻³) and mixing ratio (χ_c) for open- and closed-path, respectively, are sensitive to variations in temperature and water vapour or other effects not related to turbulent transport. They require specific adjustments in order to compute correctly eddy covariance fluxes or any other Reynolds averaging statistics including spectra and cospectra. The following expressions were used for the LGR fast methane analyzers where the subscript m , q , c and a refer to methane, water vapour, carbon dioxide and dry air, respectively:

$$\chi'_{m,nat} = \chi'_m + \frac{\bar{\chi}_m}{\bar{\chi}_a} \chi'_q \quad (2)$$

and for the LI-7500 CO₂ and H₂O analyzers:

$$\begin{aligned} \rho'_{q,nat} &= (1 + \sigma) \left(\rho'_q + \bar{\rho}_q \frac{T'}{\bar{T}} \right) \\ \rho'_{c,nat} &= \rho'_c + \frac{\bar{\rho}_c}{\bar{\rho}_a} \rho'_q + \bar{\rho}_c (1 + \sigma) \frac{T'}{\bar{T}} \end{aligned} \quad (3)$$

and for the LI-7700 CH₄ analyzer:

$$\begin{aligned} \rho_{m,r} &= \kappa(T, P_e) \rho_m \\ \rho'_{m,nat} &= \rho'_{m,r} + \frac{\bar{\rho}_{m,r}}{\bar{\rho}_a} \rho'_q + \bar{\rho}_{m,r} (1 + \sigma) \frac{T'}{\bar{T}} \end{aligned} \quad (4)$$

where the subscript *nat* refers to natural fluctuations (see Detto and Katul, 2007 for details), $\sigma = \bar{\rho}_q / \bar{\rho}_a$, over-bar indicates mean quantities and prime letters are the departure from the mean. The term $\kappa(T, P_e)$, which takes into account for spectroscopy effects, is a function of instantaneous temperature and equivalent pressure $P_e = P(1 + 0.46\chi_q)$ and is given in a look-up table or approximate analytical form (see instrument manual for details). Note that in the Eqs. (2) and (4), water vapour mixing ratio χ_q and density ρ_q needed for the correction are obtained from the LI-7500. For the 3-channels LGR analyzers, FGGA, water vapour mixing ratio can be taken from the additional channel measured in the same cell as the CH₄.

For a closed-path sensor, we assume that, when sampling air through a tube, high frequencies temperature fluctuations are dampened (Leuning and Moncrieff, 1990). Slow temperature fluctuations are captured by the thermistor (with high accuracy but slow response) located in the sampling cell and used to compute the mixing ratio. The LI-7700 is provided with a temperature sensor, but unfortunately it cannot be used to correct the gas densities

Table 1

Statistics for the two periods in Fig. 7.

	Cows in footprint	Cows outside of footprint
Length (min)	31.96	37.45
$\bar{u}$ (m/s)	1.49	1.38
u^* (m/s)	0.17	0.12
lag _{lgr} (s)	1.3	1.3
lag _{LI-7500} (s)	0.2	0.2
$\bar{w}'T'$ (°C m/s)	0.003	0.003
$\bar{w}'q'$ (mmol m ⁻² s ⁻¹)	0.041	0.039
$\bar{w}'c'$ (μmol m ⁻² s ⁻¹)	4.34	2.51
$\bar{w}'m'$ (nmol m ⁻² s ⁻¹)	128.50	-0.87

in Eq. (4) because it has not an adequate response. Instead, we used the temperature derived from sonic speed of sound after removing crosswind and humidity effects (Schotanus et al., 1983; Kaimal and Gaynaor, 1991). For the C-SAT3, the cross-wind effects are already taken into account in the instrument internal algorithm. Other density effects due to instrument self-heating are not considered important for this sensor (McDermitt et al., 2010).

2.8. Spectral losses

Eddy covariance fluxes suffer from systematic underestimations (Moore, 1986) that include: (1) sensor path line or volume averaging, (2) separation distance between sonic and gas analyzer or tube intake, (3) tubing attenuation for closed-path analyzer, especially for adsorbing species, (4) the residence time in the cell of the closed path analyser, (5) the use of digital filters, and (6) the spectral cut-off for under sampling (generally less than 10 Hz).

All these factors together produce high-frequency losses which can be represented by a proper transfer function H_{wm} . Given a true cospectrum C_{wm} defined over a frequency interval $f[0, nq]$, being nq the Nyquist frequency, the measured flux $\bar{w}'m'$ can be expressed as:

$$\bar{w}'m' = \int_0^{nq} H_{wm}(f) C_{wm}(f) df \quad (5)$$

These effects are generally treated as linear, first-order response with correspondent transfer function given by (Horst, 2000):

$$H_{wm}(f) = \frac{1 + \omega^2 \tau_w \tau_m + \omega(\tau_w - \tau_m)Q/C_{wm}}{(1 + \omega^2 \tau_w^2)(1 + \omega^2 \tau_m^2)} \quad (6)$$

where τ_w and τ_c , are the characteristic time constants related to line sonic averaging and sensor response, respectively, Q is the quadrature spectrum and $\omega = 2\pi f$. Assuming negligible Q and $\tau_m \gg \tau_w$, Eq. (6) reduces to:

$$H_{wm}(f) \simeq \frac{1}{(1 + \omega^2 \tau_m^2)} \quad (7)$$

As for the lag time, the constant τ_m depends on fixed factors, such as tube length, cell volume, separation distance, path length, and random factors, such as wind speed and direction, pump flow rate, and operating cell pressure, which can vary between analysis blocks. Because τ_c is generally unknown, it is estimated empirically on the basis of scalar similarity, comparing the normalized cospectrum with those for temperature, water vapour or carbon dioxide for which the first order time responses are known (see Massman, 2000, Table 1) or by fitting Eq. (1). Finally, a correction factor can be estimated as the ratio:

$$CF = \frac{\bar{w}'m'_{corr}}{\bar{w}'m'} = \frac{\int_0^\infty H_{wm}^{-1}(f) \hat{C}_{wm}(f) df}{\int_0^\infty \hat{C}_{wm}(f) df} \quad (8)$$

where $\hat{C}_{wm}$ is the measured cospectrum.

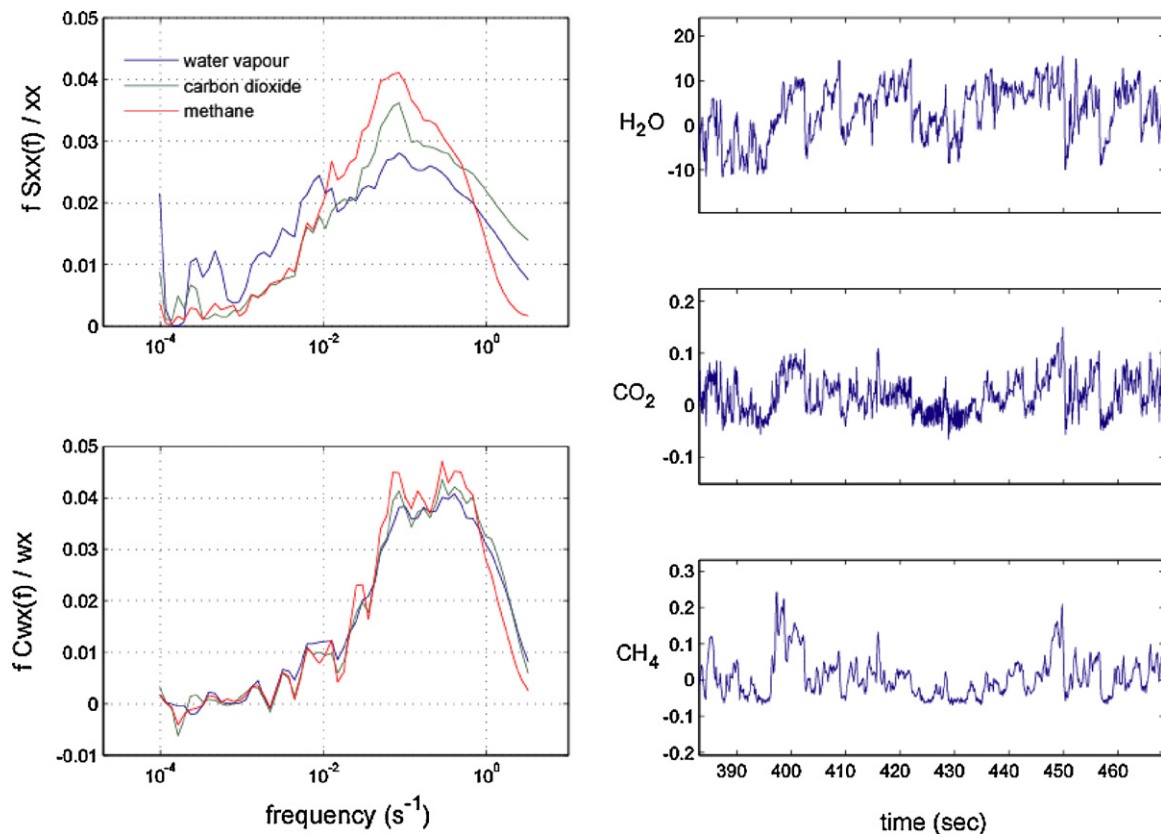


Fig. 3. Comparison of normalized spectra and cospectra of water vapour (LI-7500), carbon dioxide (LI-7500), and methane (LGR analyzer with scroll pump) (left panels) for signals of duration of approximately 3.5 h, DOY 25, 2008, Sherman Island (measurement height 3 m). All the (co)spectra are normalized so the area beneath the curve is equal to one. Note, the x-axis extends more than the usual 30 min window, allows for investigating low frequency components. The right hand panels show a sub-set of the signal used for spectral computation.

3. Results

3.1. Spectral analysis

After verifying the accuracy and stability of the instruments are adequate for eddy covariance application (Section 2.4), spectral and cospectral analysis is the next step to assess the ability of the gas analyzer to measure the turbulent activity across certain frequency ranges responsible for the vertical transport. This analysis should show the presence of an energetic band with a peak around the typical surface layer eddy size, roughly the measurement height, and power law decay, approximately $-5/3$ for spectra and $-7/3$ for cospectra.

The performance of the closed-path methane system is assessed independently here, comparing turbulent spectra and cospectra with those of water vapour and carbon dioxide measured simultaneously by sensors (LI-7500) with known responses (Fig. 3). We chose data from the peatland pasture site on January 25, 2008 because of some special circumstances: (1) the fluxes of methane were very high, greater than $300 \text{ nmol m}^{-2} \text{ s}^{-1}$, due to the presence of cows around the tower, (2) vegetation was almost absent during that period of the year and the ecosystem (soil and cattle) was a net source of carbon dioxide, which amounted to $6 \mu\text{mol m}^{-2} \text{ s}^{-1}$, (3), the wind speed was strong, averaging 5–7 m/s, with regular intensity and direction for most of the day, (4) the sky was overcast, (5) the average temperature was around 13°C , and (6) atmospheric conditions at the surface were in a neutral diabatic state. From this record, three and half hours (from 10:00 to 13:30) of quasi-stationary turbulent conditions were extracted for spectral calculation. All the data were corrected using previously described

coordinate rotation, synchronization and air density fluctuations. Linear trends in scalar concentrations were also removed.

Inspecting the signals in segments compared to the integral time scale of approximately 100 s, as in the example of Fig. 3 (left panels), we discover that the turbulent structures are clearly visible in all the tracers and perfectly synchronized with each other. The spectra and cospectra in Fig. 3 show that the energetic bands are co-located between frequencies 10^{-2} –1 Hz, which correspond to time scales equal to 1–100 s, with peaks at 0.02 Hz (50 s) for the spectra and 0.05 Hz (20 s) for the cospectra. The methane spectrum suffers from some high frequency attenuation, indicated by a steeper slope when compared to carbon dioxide and water vapour spectra.

The cospectra show more agreement, all the peaks overlap and the spectral attenuation for methane is barely visible, contributing about 10% of total area ($\text{CF} \approx 1.1$ with $\tau_m \approx 0.1 \text{ s}$), compared to carbon dioxide and water vapour. Considering that spectral losses are proportional to wind speed (Horst, 1997; Massman, 2000), which was particularly high that day, we consider in general these effects small, but not completely negligible.

Using a relatively long series, more than 3 h, compared to common eddy covariance averaging window of 20–40 min, allows us to investigate low frequency components with less uncertainty. Note, because the exceptional stationary conditions, apart from the removed linear trends, all the cospectra decay smoothly to zero. The spectra exhibit more low frequency energy, in particular water vapour, which determines their differences due to normalization, in addition to the high frequency attenuation.

This analysis confirms that our system, equipped with cavity ring down technology, is able to reproduce the basic spectral characteristics of eddy covariance fluxes, at least when compared to

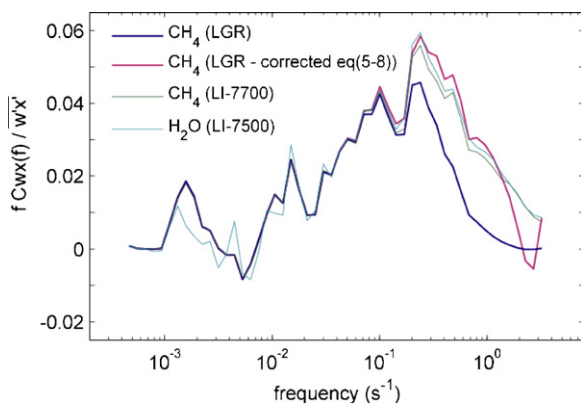


Fig. 4. Cospectra recorded above a restored wetland DOY 181, 2010 using a LGR fast gas analyzer and a diaphragm pump (flow rate 12 lpm). The corrected CH_4 cospectrum was obtained with Eqs. (5)–(8) and τ_m set to 0.35 s resulting in CF = 1.45. Cospectra measured with LI-7500 and LI-7700 are also shown for comparison.

what is established for water vapour and carbon dioxide obtained using an open-path infrared gas analyzer. It is worthwhile to notice that in general cospectra flux losses are less severe than that associated with the power spectrum because in the inertial subrange the energy decays faster for the cospectra.

When using the undersized pump, the spectral losses increase because the cell is not flushed at an adequate rate with residence of time approximately 0.4 s. In fact, repeating the analysis at the restored wetland and rice field sites, where the smaller flow diaphragm pump is used, we found substantial attenuation of the cospectra as shown as an example in Fig. 4. The expected cospectral shape can be reconstructed reasonably well, apart from introducing some noise at high frequencies, multiplying the cospectrum by a first-order transfer function (Eq. (7)) with the time constant τ_m tuned to match the cospectrum of water vapour. For this run, the flux loss amounted to 45%.

Assuming only fixed factors for τ_m , since most of the attenuation is caused by a slow but relatively constant flow rate, the correction factor for the fluxes is linearly and tightly correlated with mean wind speed. For higher wind speed, the (co)spectral peaks are shifted towards higher frequencies, making the spectral losses more severe. This can be shown, without using an analyt-

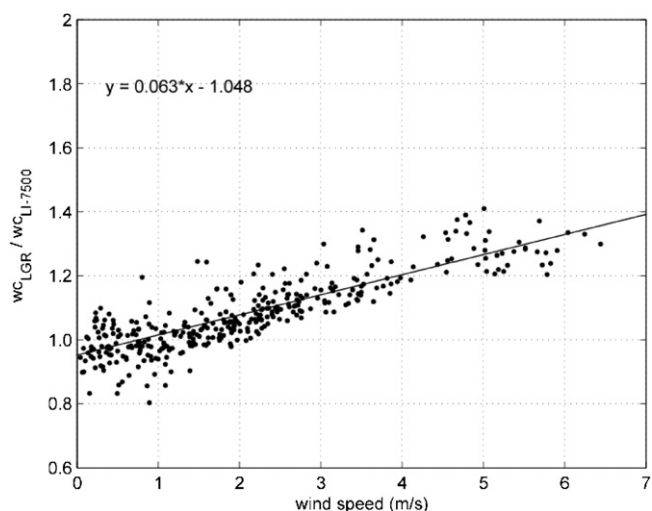


Fig. 5. Correction factor between CO_2 fluxes ($\overline{w'c'}$ > $\text{mmol m}^{-2} \text{s}^{-1}$) measured above the rice field using a 3-channel LGR analyzer with a diaphragm pump (flow rate 15 slpm) and a LI-7500 (May–December, 2009). Note that for very low wind speeds, the flux attenuation becomes negligible.

ical model, by taking advantage of the additional CO_2 channel of the closed-path sensor at the rice field site. A correction factor is then computed assuming the CO_2 flux computed from the LI-7500, which is not affected by the slow flow rate, as the 'true' flux (Fig. 5).

3.2. Air density adjustments

As previously mention, air density fluctuations were removed from the tracer measurements before calculating any statistics. For a closed path system, the methane flux is affected only by water vapour flux. From Eq. (2), we can derive:

$$\bar{\rho} \overline{w' \chi'_{m, \text{nat}}} = \bar{\rho} \overline{w' \chi'_m} + \bar{\rho} \overline{\chi'_m \frac{w' \rho'_q}{\bar{\rho}_a}} \quad (9)$$

When considering a range of latent heat between 0 and 400 W m^{-2} or when $\overline{w' \rho'_q}$ is $0\text{--}9 \text{ mmol m}^{-2} \text{s}^{-1}$, and an average atmospheric methane mixing ratio equal to 2 ppm, the second term on the right hand side of Eq. (9) ranges between 0 and $18 \text{ nmol m}^{-2} \text{s}^{-1}$. Thus

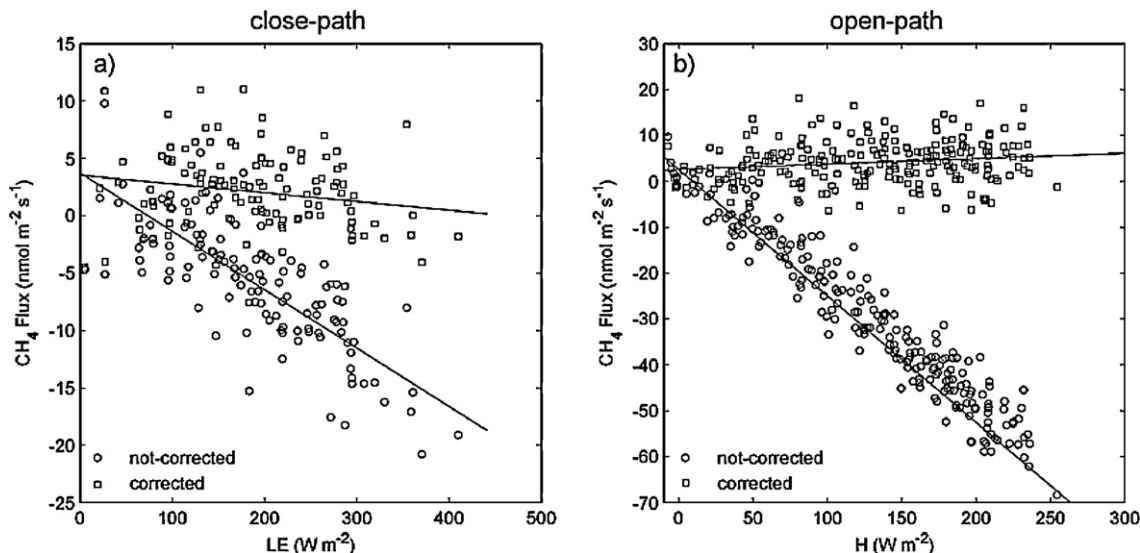


Fig. 6. (a) Dependence of CH_4 flux on latent heat (LE) with or without air density adjustments from data recorded between April and June, 2007 at peatland pasture using the closed-path system (LGR and scroll pump). (b) Dependence of CH_4 flux on sensible heat (H) with or without air density adjustments for data recorded June 2010 at peatland pasture with LI-7700 open-path system.

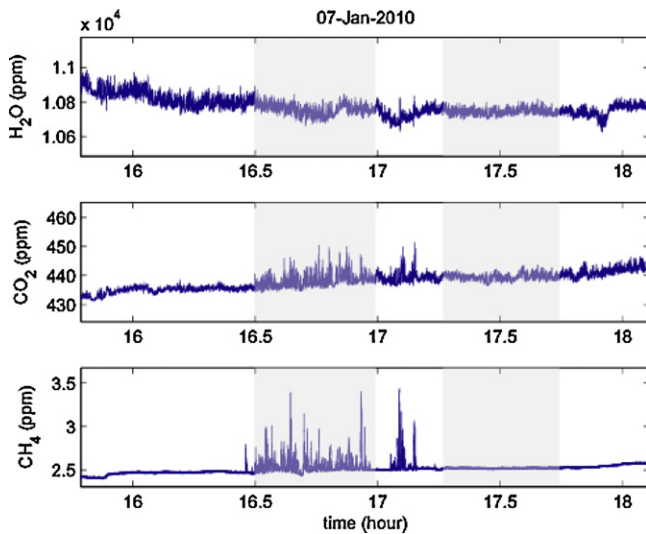


Fig. 7. Greenhouse gases mixing ratio measured simultaneously on DOY 7 2010 at peatland pasture during a passage of cows. Shaded areas indicate periods used for subsequent analysis.

this term becomes important for small fluxes, as were measured at the peatland pasture site in the absence of cattle.

For the above analysis, the runs were selected by visual inspection, between April and June 2007, during a rain free period with almost constant soil moisture conditions. Signals of variable window size (from 20 to 60 min) were extracted for periods when the cows were in the far fetch; we assume they had a marginal effect

on the methane fluxes because the methane concentrations did not present any evident sign of non-stationarity, abrupt changes, waves or other complex dynamics. The fluxes from these periods were associated with very low and constant emissions from the peat soil, as confirmed by independent weekly measurements along a 100 m transect of five static chambers, in front of the tower (Teh et al., 2011). The average from the chambers for this period was $4 \text{ nmol m}^{-2} \text{ s}^{-1}$.

Fig. 6 (panel a) shows that there is clear dependence of CH_4 flux (not density-adjusted) on latent heat, almost linear, as predicted by Eq. (9), with many negative values up to $-20 \text{ nmol m}^{-2} \text{ s}^{-1}$ caused by higher evapotranspiration rates. The air density adjustment corrects this bias, but the slope is still slightly negative. The intercept of the linear regression in Fig. 6a is equal to $4 \text{ nmol m}^{-2} \text{ s}^{-1}$ and the average corrected fluxes equal $2 \text{ nmol m}^{-2} \text{ s}^{-1}$, which are in good agreement with the chamber measurements.

As mentioned above, the open-path system is more dependent on fluctuations in air density related mostly to sensible heat, as clear also from Eq. (4). However, a derivation analogous to Eq. (9) is analytically more complex and it is not provided here. The scatter plot of the uncorrected and corrected fluxes versus sensible heat, Fig. 6b, shows a strong dependence of the uncorrected flux that can reach up to $-70 \text{ nmol m}^{-2} \text{ s}^{-1}$ for values of sensible heat equal to 250 W m^{-2} . Also in this case, the correction works well despite some positive residual slope (which may be real).

A possible source of errors for this analysis may arise because the water vapour concentrations were not measured at the same point as the methane measurements, but derived from the LI-7500 open-path IRGA and the temperature fluctuations from sonic speed of sound, which in turn are affected by errors as well. In addition, the water vapour fluctuations may be attenuated in the tube and

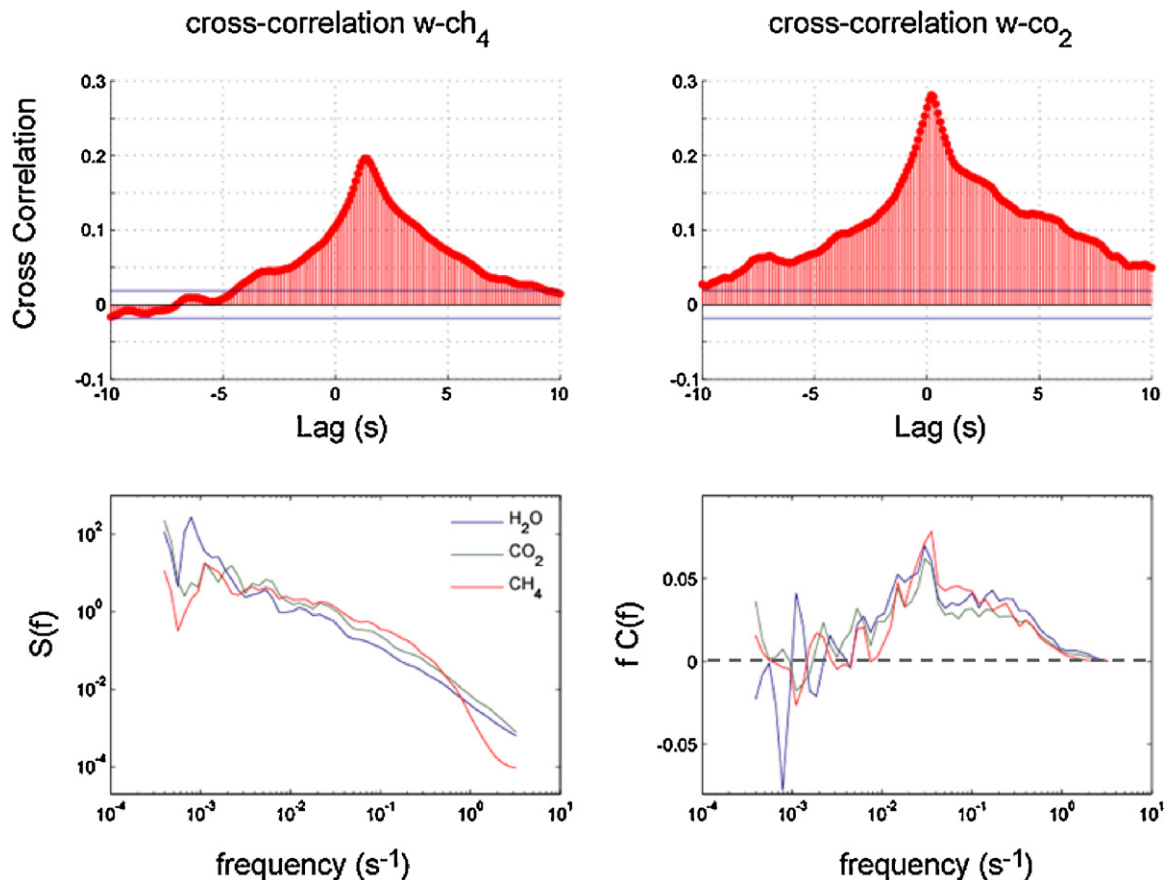


Fig. 8. Cross-correlation and spectral analysis of a period identified with cows present in the near fetch of the tower. CH_4 is measured with LGR-analyzer and $\text{CO}_2/\text{H}_2\text{O}$ with LI7500.

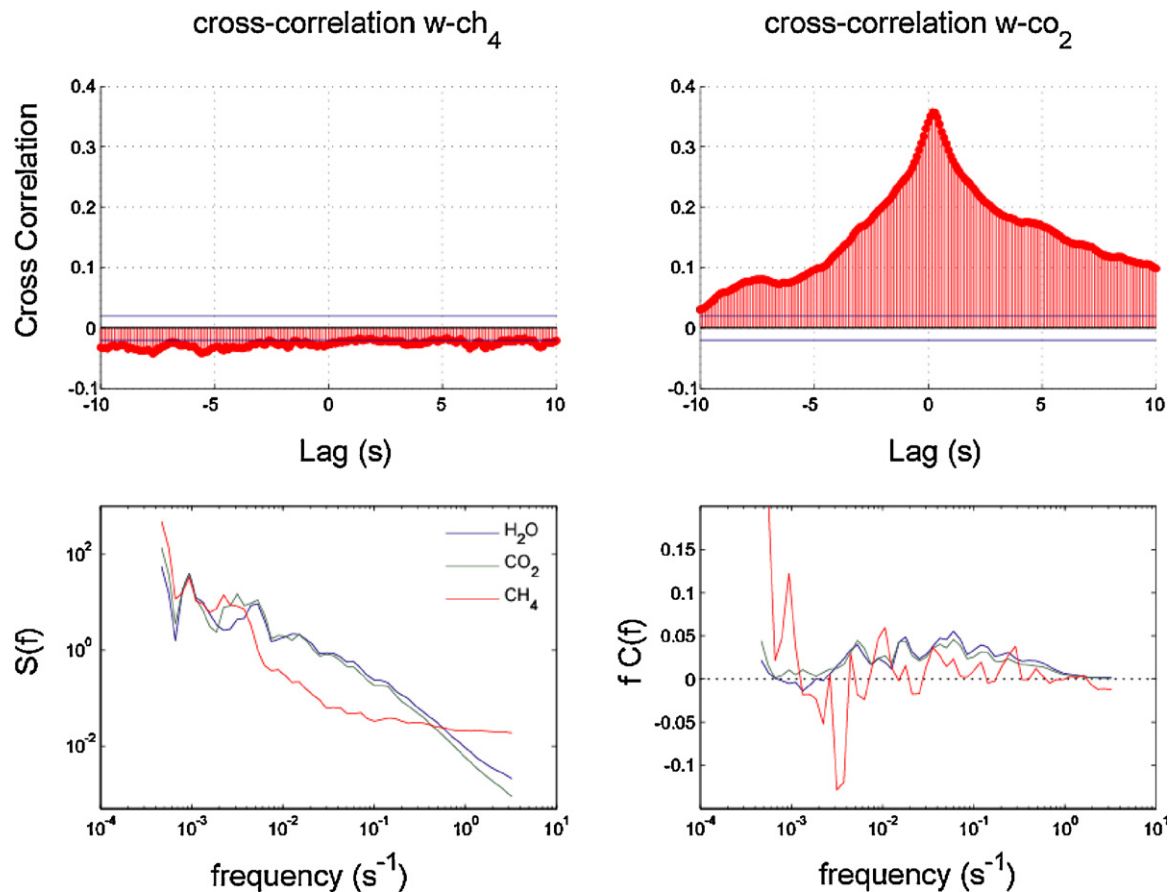


Fig. 9. Cross-correlation and spectral analysis of a period immediately after the cows have left the near fetch of the tower.

a phase shift with methane may occur (Ibrom et al., 2007) for the closed-path LGR analyzer. The 3-channel LGR analyzers have the ability to measure water vapour mixing ratio simultaneously in the same cell as CH_4 . The fluxes corrected using the internal water vapour, were about the same of those corrected with the LI-7500 (data not shown).

It is obvious that the correction term adds more uncertainty to the overall flux estimation. Given that the major contributions to the correction terms derive from latent heat and sensible heat for a closed- and open-path, respectively, it is straightforward to assess the uncertainty in the density adjustment once the uncertainty in latent and sensible heat are known. We adopt the values of 25.3 W m^{-2} and 22.7 W m^{-2} for sensible and latent heat, respectively, estimated by Hollinger and Richardson (2005) using a two-tower approach (see their Table 1). For a closed-path, from Eq. (9), the uncertainty due to flux adjustment amount to $\sim 1 \text{ nmol m}^{-2} \text{ s}^{-1}$. For an open-path, using the regression in Fig. 7 we obtain a value of $\sim 7 \text{ nmol m}^{-2} \text{ s}^{-1}$.

3.3. Minimum detectable flux

With natural variability in turbulence, scalar concentration fluctuation, sensor noise and detection limit, it is important to know whether the observed flux is significantly different from zero, or not. When fluxes are close to or below the minimum detectable limit, it would be very difficult to find meaningful correlations between vertical velocity and the scalar concentrations. If a clear peak in the cross-correlation function does not emerge, the evaluation of the time lag becomes problematic, casting further doubt on the estimate of the fluxes.

Fig. 7 shows an example comparing two runs selected by visual inspection during a time when the cows were within the instrumentation footprint and immediately after. In the first period the methane flux was greater than $100 \text{ nmol m}^{-2} \text{ s}^{-1}$ and the cross-correlation shows a clear peak at 1.3 s (Fig. 8). The corresponding value of the correlation coefficient for this lag exceeds many times the 95% confidence interval if the two series are completely uncorrelated, and it is just slightly smaller than the corresponding correlation of coefficient between the vertical wind and CO_2 . The spectral analysis in Fig. 8 (bottom panels) shows similar results for the previous example (Fig. 3), with high frequency attenuation in CH_4 -spectrum, but substantial agreement of the methane-cospectrum with the other scalars.

The period immediately after the passage of cows is indicated by a decrease in the variance, but not necessarily of the background concentrations as the wind conditions were almost the same, see Table 1. Fig. 9 shows that the analysis, in this case, produces different results. The cross-correlation function between vertical velocity and methane is barely significant at 95% confidence interval and does not present an unambiguous peak as evident in the vertical wind and carbon dioxide cross-correlation. Using the value 1.3 s for the lag time, estimated from the previous period, we obtain a flux equal to $-0.8 \text{ nmol m}^{-2} \text{ s}^{-1}$. The methane-spectrum, instead of spectral loss, exhibits noise for frequencies greater than 10^{-2} Hz , thus affecting all the turbulence scales. The methane-cospectrum appears much noisier than other scalars and low-frequency components are predominant in determining the sign of the flux.

The minimum detectable flux cannot be treated as a deterministic value, but it varies with sensor performance, specific instrumental set-up (tube length, measurement height, etc.), and atmospheric conditions such as turbulence. Considering the maxi-

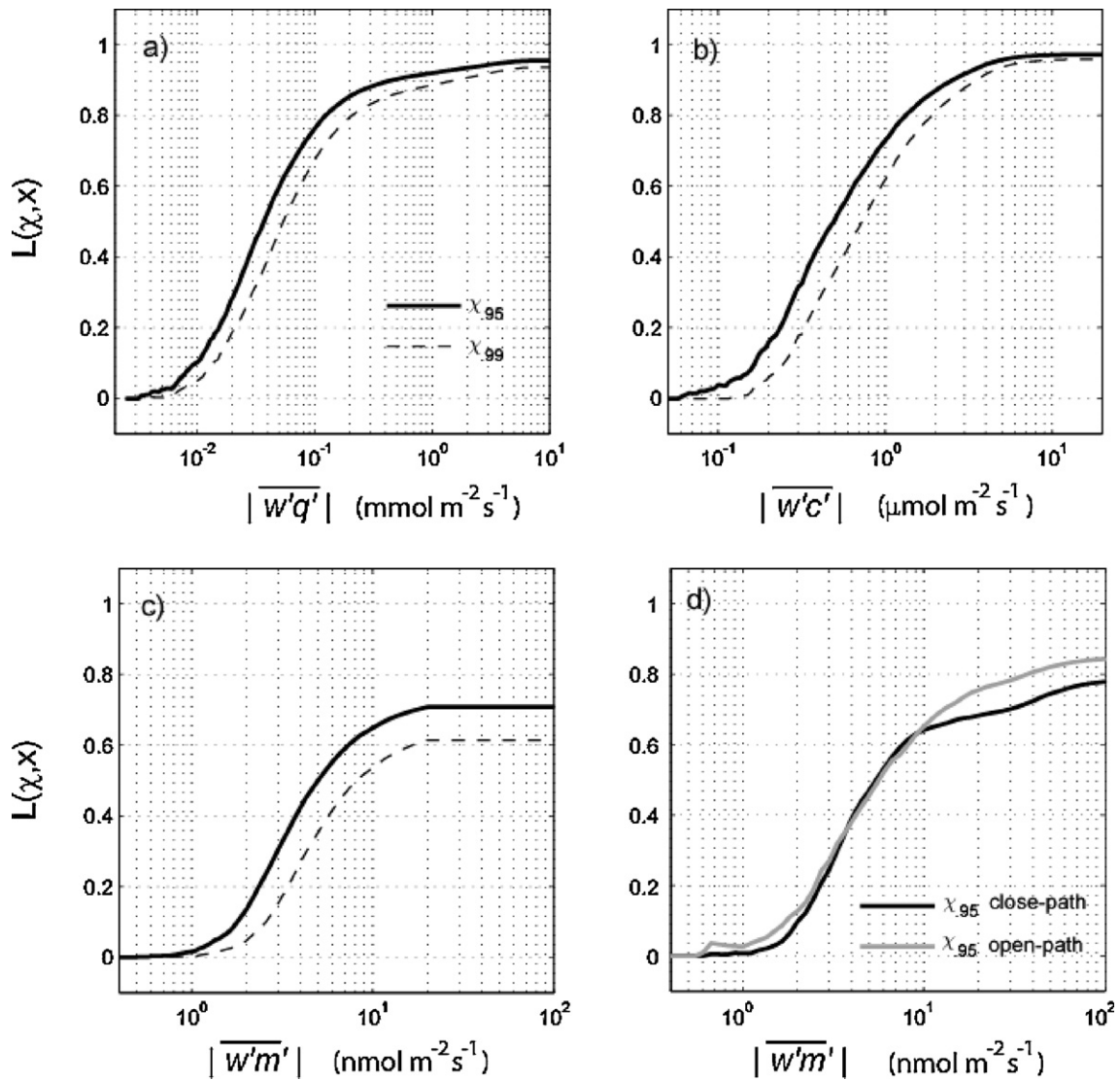


Fig. 10. Estimation of the probability that the maximum correlation function between vertical wind and water vapour (a), carbon dioxide (b), or methane (c), is significant at the 95% confidence interval (thick line) and 99% (dashed line) as function of the logarithmic flux magnitude (data from Sherman Island, 2007–2010). The likelihood functions of methane fluxes obtained when both LI-7700 and LGR analyzers were operative are shown in panel (d) (data from the three sites, May–August 2010).

imum of the cross-correlation as the discriminating statistic, χ , we define the likelihood of encountering a significant flux ($\chi \geq \bar{\chi}$), as a function of the flux magnitude, $x = |\overline{w'c'}|$ as:

$$\ell(\chi|\bar{\chi}) = P(\chi \geq \bar{\chi} | \bar{\chi} - \Delta x \leq x \leq \bar{\chi} + \Delta x) \quad (10)$$

For calculation purposes, it is easier to rewrite the probability in Eq. (10) in cumulative terms:

$$L(\chi|\bar{\chi}) = P(\chi \geq \bar{\chi} | x \leq \bar{\chi}) \quad (11)$$

where the critical value $\bar{\chi}$ is taken on the null hypothesis that vertical velocity and the tracer are uncorrelated with significance level $1 - \alpha$. Assuming for simplicity that the two processes are Gaussian, this is $\bar{\chi} = t/\sqrt{N-2} + t^2$, where N is the number of data points (18,000 for a 30-min window) and t is the inverse of Student's t cumulative distribution function with $N-2$ degrees of freedom for the corresponding probabilities α (two-tailed test).

The results of this analysis are presented in Fig. 10, using a longer term dataset of more than 3 years collected at the peatland pasture site for water vapour, carbon dioxide and methane fluxes calculated for a 30 min window. $L(\chi|x)$ shows that for small fluxes the probability to find a significant correlation is small and this probability

increases with greater flux values. In order to define a minimum detectable flux, consistent for each tracer, we choose the value correspondent to the inflection point of the likelihood curve or the maximum of the derivative of $L(\chi|x)$. This critical point defines the regions where an increase in flux magnitude corresponds to a decrease in the improvement of $L(\chi|x)$.

The values correspondent to the inflection points, obtained using a differential operator, are $0.035 \text{ mmol m}^{-2} \text{ s}^{-1}$, $0.31 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$ and $3.78 \text{ nmol m}^{-2} \text{ s}^{-1}$ for water vapour, carbon dioxide and methane flux, respectively, at 95% confidence interval. These values represent the minimum detectable flux that is likely to be significant and include not only instrument limitations, but also the ability to process the data in 'real world' situations, such as the detection of the lag time, de-spiking, corrections, and other site-specific considerations, such as the presence of low frequency effects induced by heterogeneity or non-stationarity which might affect cross-correlation and cospectral functions. Interestingly, the likelihood functions obtained for the open- and closed-path system, when both were operating simultaneously, are very similar (Fig. 10d), indicating that the two systems have very comparable performance for small fluxes.

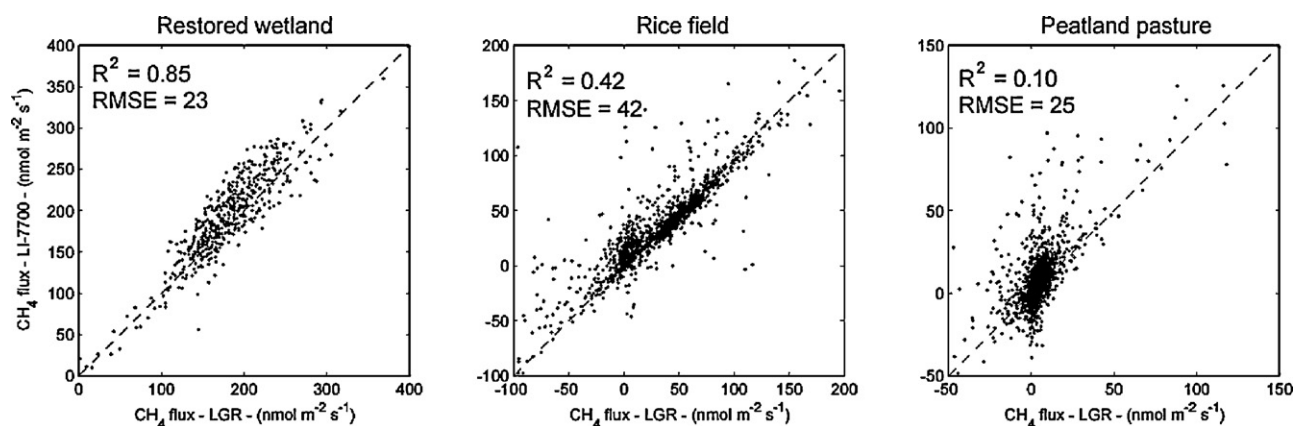


Fig. 11. Comparison between CH_4 fluxes obtained from the open- and closed-path sensors at the three sites (restore wetland, rice field, and peatland pasture) during May–August 2010. Coefficients of determination and root mean square errors (in $\text{nmol m}^{-2} \text{s}^{-1}$) are also reported.

The minimum flux for water vapour is very small, in energetic units equal to 1.55 W m^{-2} , but realistically, if we look at how well-defined the cospectra are in the previous two examples, Figs. 8 and 9, compared to the small flux magnitude (Table 1). Also, note that for methane, $L(\chi|x)$ does not reach a value of one asymptotically, as the other scalars do. This is due to the large amount of small fluxes that are not significantly different from zero.

This analysis should not be confused with the flux uncertainty, which is an estimation of the total measurement error (Hollinger and Richardson, 2005), which in general is larger than the minimum detectable flux. Recently, Billesbach (2011) developed a method based on Monte Carlo simulation to estimate the flux uncertainty due to instrumental noise only. The method is fairly easy to implement and the results of this analysis are presented in Table 2.

3.4. Open- and closed-path comparisons

Finally, we compare the methane fluxes obtained from the open- and closed-path systems for the three ecosystems using 4 months of measurements during which the LI-7700 was moved from one site to another every 2–3 weeks, see Fig. 11. At the rice field and restored wetland sites, the surface was flooded, so the sensible heat was smaller than latent heat, and the CH_4 emissions vary one order of magnitude among the two locations; the rice field was a moderate source, approximately $30(\pm 55) \text{ nmol m}^{-2} \text{s}^{-1}$ and the restored wetland was a larger source, approximately $190(\pm 60) \text{ nmol m}^{-2} \text{s}^{-1}$. The scatter plots show generally good agreement between the two estimates in terms of magnitudes with more scatter at the rice field. At the peatland pasture site, the surface was relatively dry and the available energy was equally partitioned between latent and sensible heat. The soil was a small CH_4 source, $5(\pm 13) \text{ nmol m}^{-2} \text{s}^{-1}$, excluding sporadic large fluxes during passages of cows. The scatter at the peatland pasture, not surprisingly for such small fluxes, is larger.

In order to assess independently the role of the pump size on the comparison between open- and closed-path systems, we select

runs from the peatland pasture (where a fast pump was used) and from the rice field (where a slow pump was used) with comparable flux magnitude. The fast pump over performed slightly the slow pump in term of R^2 (0.17 against 0.15) and root mean square errors (6.8 against $8.6 \text{ nmol m}^{-2} \text{s}^{-1}$) indicating that a slow pump adds further uncertainty to the flux estimates.

4. Discussion and conclusion

Open-path and closed-path gas analyzers are two alternatives employed in eddy covariance applications for CO_2 fluxes and, very recently, CH_4 . Although in theory the differences in the principle of measurement do not imply a preference for the type of gas analyser to be used, the two systems have remarkably distinct features, which require special care in the data processing.

In our experiments, for example, the time lags, for the open-path system were approximately constant at 0.1 and 0.9 s for LI-7500 and LI-7700, respectively, with small influences from wind speed and direction. For the LGR analyzers (closed-path), the time lags were approximately 1.1 and 2.2 s using the fast and slow pump, respectively, but more variable, due to variation of the flow rate, than the open-path sensors and in many cases difficult to detect. The two methods for evaluating the lag, maximum cross-correlation and total phase shift were in good agreement.

For small fluxes (relatively to latent heat) measured with a closed-path, the air density adjustments for water vapour fluctuations become important, switching in some cases from a sink to a source. Considering, for example, that estimates from northern American wetlands, one of the ecosystems responsible for methane emission on a global scale, are approximately $7.6 \text{ g CH}_4 \text{ m}^{-2} \text{yr}^{-1}$ ($15 \text{ nmol m}^{-2} \text{s}^{-1}$) (Bridgman et al., 2006), it is mandatory that these adjustments are applied correctly, as also observed by Smeets et al. (2009).

When the site location is lacking power facilities, an undersized pump needs to be used with consequently spectral loss that can amount to 40% in high wind conditions for our set-up (4 m tube and 3 m tower). Although in principle it is always possible to correct for flux losses, spectral methods rely on well-defined cospectral shapes. In the case of small fluxes spectra and cospectra can be very noisy as we have shown in some of the examples above. For a multi-channel sensor the attenuation for methane is nearly equal to carbon dioxide. Instead of using the computationally intensive spectral analysis, we corrected the long term record of methane fluxes based on the ratio between carbon dioxide fluxes obtained by the open- and closed-path systems. At the rice field site, after applying this correction, the average methane flux changed from 7.1 to $8.7 \text{ nmol m}^{-2} \text{s}^{-1}$, over 400 days of measurements.

Table 2

Minimum detectable flux and instrumental flux uncertainty (Billesbach, 2011), for the three tracer fluxes recorded at Sherman (2007–2010). Data for the LI-7700 (last row) are only for May–August 2010.

	Minimum detectable flux	Instrumental flux uncertainty
$\overline{w'q'}$ ($\text{mmol m}^{-2} \text{s}^{-1}$)	0.035	0.015
$\overline{w'c'}$ ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	0.31	0.066
$\overline{w'm'_{\text{LGR}}}$ ($\text{nmol m}^{-2} \text{s}^{-1}$)	3.78	1.29
$\overline{w'm'_{\text{LI-7700}}}$ ($\text{nmol m}^{-2} \text{s}^{-1}$)	3.41	1.14

First impression made us sceptical about the potential attenuation of the LI-7700 because of relatively larger size, but detailed data analysis revealed that this open-path analyzer did not suffer from excessive spectral loss, at least when cospectra are compared with water vapour and carbon dioxide, despite the path volume of LI-7700 being much greater than LI-7500. The smaller power requirement from the LI-7700 partially offsets the greater dependence on density adjustments and line broadening in addition to the classical WPL corrections. However, this correction inevitably affects the precision of the flux estimates, depending also on temperature and water fluxes, which propagate their respective errors into flux computation.

Unfortunately, even for moderate fluxes these corrections become comparable or even greater in order of magnitude than the measured (not corrected) fluxes. Under these conditions, it is recommended to check the consistency of the estimates during a time of the day when energetic fluxes are close to zero, i.e. sunrise, sunset, and night-time with small radiative cooling, so the air density effects are minimized. Because water and temperature fluxes have strong diurnal pattern, this may prevent estimating small methane diurnal changes with confidence.

For small emissions/sinks, the precision of the sensor becomes the limiting factor in detecting fluxes and this analysis shows the two systems are very comparable. A further complication arises for the closed-path system in determining the correct time shift to synchronize gas and sonic anemometer measurements. This problem seems to not affect the open-path system, which has a more stable time lag. In addition, raw signals contain density air effects that in most cases increase the correlation with vertical velocity and may help to correctly detect peaks in the cross-correlation functions, computed before adjusting the fluctuations for density effects.

Closed-path systems require more intensive care in cleaning of filters and optics, maintaining pumps, and plumbing. During three and more years of continuous experiments, we experienced wear and tear of the pumps mechanical parts, with a major breakdown during hot summer months, which convinced us to use an air-cooling system to prevent overheating, requiring additional power. Dew accumulates in water traps during the winter and filters need to be swapped often in the dusty peat environment during the dry months, to maintain clean optics and avoid the restriction of inflow. The LGR analyzers use an internal bypass valve, which needs to be adjusted manually to allow a pressure controller to handle a large range of flow rates to insure optimal cell operating pressure (a problem that occurs more often with the small pump). During the 3 years of experiment at Sherman the loss of data from instrument malfunctioning amounted to 18% (this excludes data loss by quality check assessment). From the little experience we have had with the LI-7700, the open path seems more appropriate for unattended sites, due to its low power requirement and more so because an automated mirror cleaning system is available. However, fog and rain, very frequent during winter months in the Sacramento-San Joaquin Delta, and bird excrement, limit the applicability of the open path and this aspect should be taken into consideration if the sites (especially wetland sites) experience this type of meteorological conditions. Data loss for instrument malfunctioning amounted to 7% (comparing to 16% of the LGR during the same period).

Finally, this study shows how methane fluxes are very sensitive to disturbances. The presence of livestock or other anthropogenic sources, such as fuel combustion machineries, oil refineries, and landfills, may compromise the estimates of the soil methane budget. Because the extension and the orientation of the flux-footprint changes with boundary layer dynamics, daily and seasonal patterns can be distorted, with negative effects not only on the estimates of budgets, but also on relations with other environmental factors

which regulate methane production and consumption in the soil, e.g., temperature, soil moisture, and water tables.

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