

Evaluation of Density Corrections to Methane Fluxes Measured by Open-Path Eddy Covariance over Contrasting Landscapes

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Abstract Corrections accounting for air density fluctuations due to heat and water vapour fluxes must be applied to the measurement of eddy-covariance fluxes when using open-path sensors. Experimental tests and ecosystem observations have demonstrated the important role density corrections play in accurately quantifying carbon dioxide (CO₂) fluxes, but less attention has been paid to evaluating these corrections for methane (CH₄) fluxes. We measured CH₄ fluxes with open-path sensors over a suite of sites with contrasting CH₄ emissions and energy partitioning, including a pavement airfield, two negligible-flux ecosystems (drained alfalfa and pasture), and two high-flux ecosystems (flooded wetland and rice). We found that density corrections successfully re-zeroed fluxes in negligible-flux sites; however, slight overcorrection was observed above pavement. The primary impact of density corrections varied over negligible- and high-flux ecosystems. For negligible-flux sites, corrections led to greater than 100% adjustment in daily budgets, while these adjustments were only 3–10% in high-flux ecosystems. The primary impact to high-flux ecosystems was a change in flux diel patterns, which may affect the evaluation of relationships between biophysical drivers and fluxes if correction bias exists. Additionally, accounting for density effects to high-frequency CH₄ fluctuations led to large differences in observed CH₄ flux cospectra above negligible-flux sites, demonstrating that similar adjustments should be made before interpreting CH₄ cospectra for comparable ecosystems. These results give us confidence in CH₄ fluxes measured by open-path sensors, and demonstrate that density corrections play an important role in adjusting flux budgets and diel patterns across a range of ecosystems.

Keywords Carbon dioxide flux · Density correction · Eddy covariance · Greenhouse gas emission · Micrometeorology

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1 Introduction

Atmospheric methane (CH_4) concentrations are rising, and recent increases have been attributed to enhanced biogenic wetland emissions (Kirschke et al. 2013; Nisbet et al. 2016). Ecosystem-scale CH_4 flux measurements by eddy covariance are now possible following the development of fast response open-path CH_4 sensors (McDermitt et al. 2011), and the low power requirement of these sensors has allowed for the deployment of off-grid eddy-covariance towers at a growing number of remote wetland sites where CH_4 is produced (Baldocchi 2014). While eddy covariance provides a powerful tool to further our understanding of ecosystem greenhouse gas dynamics, a number of corrections are required to measure fluxes accurately using this method (Foken et al. 2012). Flux correction and quality control procedures have been described and evaluated extensively for CO_2 fluxes, but less attention has been paid to the evaluation of CH_4 flux corrections to date. A more rigorous appraisal of these flux corrections is warranted given the proliferation of eddy-covariance sites measuring CH_4 fluxes (Nicolini et al. 2013; Petrescu et al. 2015).

Large errors in measured fluxes potentially arise when using open-path analyzers because apparent trace gas fluxes are induced by air density fluctuations due to heat and water vapour fluxes. These errors occur because open-path analyzers measure gas densities (mmol m^{-3}) in the free atmosphere, where the external effects of sensible heat (H) and water vapour fluxes create measurable gas density fluctuations. Assuming no sources or sinks of dry air, these errors can be corrected by accounting for the small vertical velocity and convective gas flux induced by heat and water vapour fluxes using the corrections due to Webb et al. (1980) and Leuning (2007). These corrections, hereafter referred to as 'density corrections', are particularly important because they can be of opposite sign and of similar magnitude as the measured gas flux itself (Leuning et al. 1982; Foken et al. 2012), and can alter daily CO_2 fluxes up to 80% in natural ecosystems (Ham and Heilman 2003).

A number of experimental studies have evaluated density corrections to CO_2 fluxes and concluded that the theory is robust, despite the argument for alternative approaches over the years (Kramm et al. 1995; Paw et al. 2000; Fuehrer and Friehe 2002; Liu 2005; Kowalski 2006; Lee and Massman 2011). Leuning et al. (1982) demonstrated that density corrections successfully re-zeroed CO_2 fluxes over an arid, vegetation-free field. Ham and Heilman (2003) went further to test density corrections over a pavement surface and found they successfully re-zeroed CO_2 fluxes where apparent CO_2 uptake by pavement was observed during periods of positive sensible heat flux. Kondo and Tsukamoto (2008) later reproduced a similar pavement experiment and found good agreement to Ham and Heilman (2003), with some noted overcorrection due to differences in the performance of sensors measuring high-frequency CO_2 and sensible heat fluxes. While past studies have evaluated the quality of open-path and closed-path CH_4 eddy-covariance measurements (Tuzson et al. 2010; Detto et al. 2011; McDermitt et al. 2011), only two assessments of density corrections to open-path measured CH_4 fluxes have been carried out to date. McDermitt et al. (2011) demonstrated that density corrections perform well for CH_4 fluxes measured by open-path systems over zero-flux agricultural fields, and Iwata et al. (2014) evaluated the impact of the corrections to CH_4 flux magnitudes from rice. Unlike the studies assessing CO_2 -flux-density corrections, no research has evaluated density corrections to CH_4 fluxes over pavement surfaces and a wide variety of natural ecosystems. Independent assessments of CH_4 -flux-density corrections are warranted given the body of work critical of the original Webb et al. (1980) density correction (Kramm et al. 1995; Paw et al. 2000; Fuehrer and Friehe 2002; Liu 2005) and the growing number of studies using open-path CH_4 eddy-covariance measurements.

The objectives of this study are, (1) to evaluate the performance of CH₄-flux-density corrections over zero-flux sites, (2) to evaluate the relative contribution of density corrections due to heat and water vapour fluxes across a range of ecosystems with varied energy partitioning, and (3) to evaluate the influence of density corrections on daily CH₄ budgets and diel patterns across flooded high-flux and drained negligible-flux ecosystems. We measured eddy-covariance fluxes from a pavement airfield as a known zero-flux site, an alfalfa field and old pasture with low water tables as negligible-flux sites, and a restored wetland and flooded rice paddy as high-flux sites. For the pavement airfield zero-flux test case, we compared the corrected open-path CH₄ fluxes to fluxes measured simultaneously with a closed-path system to assess the quality of density corrections. Here, the closed-path system should be unaffected by high-frequency temperature fluctuations due to dampening within the sampling tube (Leuning and Moncrieff 1990), and the influence of water vapour fluxes on closed-path measurements is negligible over pavement with zero water vapour flux.

2 Methods

2.1 Study Sites and Instrumentation

We measured eddy-covariance fluxes of CO₂, CH₄, H₂O, and sensible heat above a pavement airfield where CO₂, CH₄, and H₂O fluxes were assumed to be negligible, and a variety of ecosystems (alfalfa, rice, pasture, and restored wetland) in the Sacramento–San Joaquin Delta region of California, USA. Airfield flux measurements were conducted at the Moffett Federal Airfield (Santa Clara County, California) operated by the NASA Ames Research Center where eddy-covariance flux measurements were conducted for six days from 23 to 29 September 2010. The tower was located 35 m west of the north-west corner of an airplane hanger (Hanger 2; height = 52.1 m) and was surrounded by pavement for at least 77 m on all sides (N 37°25.03320', W 122°02.71680'). The pavement surface was a mixture of asphalt (for minor interconnecting roadways) and concrete (for major runways), and CH₄ emissions should be near-zero from these surfaces (Tyler et al. 1990). During the daytime, the wind direction was predominately from the north-east (median wind direction = 047°) at a mean speed of 1.6 m s⁻¹, and pavement extends for at least 320 m in that direction. At a height of 2.5 m and 10-Hz intervals, we measured three-dimensional velocity with a sonic anemometer (WindMaster Pro, Gill Instruments, Hampshire, UK), and CO₂, CH₄, and H₂O concentrations with open-path infrared gas analyzers (LI-7500A and LI-7700, Licor Inc., Lincoln, Nebraska, USA) and a closed-path analyzer (FGGA, Los Gatos Research, Mountain View, California, USA). Gas samples were drawn to the closed-path analyzer through 5.25 m of tubing using a diaphragm pump (KNF, Trenton, New Jersey, USA) and a 2- μ m filter. All of the above data were logged to a CR1000 datalogger (Campbell Scientific, Logan, Utah, USA).

We also measured ecosystem fluxes from a network of eddy-covariance towers located in the Sacramento–San Joaquin Delta region of California, USA. Towers were installed in an alfalfa (*Medicago sativa*) field (N 38°05.94840', W 121°29.95740'; measurement height (z) = 3.90 m), an abandoned pasture dominated by *Lepidium latifolium* (N 38°02.21484', W 121°39.18558'; Ameriflux site US-Sne; z = 5.61 m), a flooded rice (*Oryza sativa*) paddy (N 38°06.52284', W 121°39.18558'; Ameriflux site US-Twt; z = 3.25 m), and a restored wetland (N 38°02.99400', W 121°45.89940'; Ameriflux site US-Myb; z = 5.44 m). All sites are located in a Mediterranean climate, and more detailed site descriptions of the pasture,

rice, and restored wetland site can be found in Baldocchi et al. (2016), Knox et al. (2016), and Sturtevant et al. (2016), respectively. Drained ecosystem fluxes should be near-zero due to oxic soil conditions inhibiting methanogenesis and promoting methanotrophy (Conrad 2007; Chamberlain et al. 2016), and positive CH₄ fluxes have been previously observed from rice and restored wetlands in the Delta region (Knox et al. 2015, 2016). At all sites, we measured three-dimensional wind velocity with sonic anemometers (WindMaster Pro, Gill Instruments, Hampshire, UK), and CO₂, CH₄, and H₂O concentrations with open-path infrared gas analyzers (LI-7500A and LI-7700, Licor Inc., Lincoln, Nebraska, USA) at 20 Hz, and high-frequency data were logged to LI-7550 data loggers (Licor Inc., Lincoln, Nebraska, USA). Corrections were applied to high-frequency vertical velocity data prior to any flux processing at all sites where WindMaster Pro firmware was affected by the ‘w bug’. This bug leads to an underestimate of vertical velocity when left uncorrected. Corrections were applied for the pasture, rice, and wetland sites, but were not required for anemometers used at the airfield and alfalfa sites. For the alfalfa, pasture, and wetland site, we report fluxes for a 14-day period from 17 to 31 August 2016, when biological activity was greatest. For the rice site, we report fluxes for a 14-day period from 27 July to 10 August 2016. We used an earlier period for the rice analysis because the rice field was being drained during the period when the other three sites were used. We chose these four sites to represent a range of energy partitioning from sites dominated by latent heat fluxes (rice and restored wetland) to those dominated by sensible heat fluxes (alfalfa and pasture), and a range of high CH₄ flux (rice and restored wetland) to negligible CH₄ flux sites (alfalfa and pasture).

2.2 Flux Processing and Corrections

Half-hourly fluxes were calculated from the covariance of vertical velocity (w ; m s⁻¹) and scalars, including temperature (T ; K) and molar densities (mmol m⁻³) of water (ρ_q), CO₂ (ρ_c), and CH₄ (ρ_m). Spikes and poor quality readings were removed from high-frequency data, and coordinate rotations were applied to half-hourly fluxes as described in Knox et al. (2015). We then applied density corrections to CO₂ and H₂O fluxes according to Eqs. 24 and 25, respectively, in Webb et al. (1980), and we used the following version for CH₄ fluxes according to McDermitt et al. (2011),

$$F_m = A \left[w' \rho'_m + B \frac{\bar{\rho}_m}{\rho_a} w' \rho'_q + C \left(1 + \frac{\bar{\rho}_q}{\rho_a} \right) \frac{\bar{\rho}_m}{\bar{T}} w' T' \right] \quad (1)$$

where F_m is the corrected CH₄ flux (mol m⁻² s⁻¹), ρ_a is the molar density of dry air (mol m⁻³), and A , B , and C are coefficients calculated from T , air pressure, and ρ_q using parametric equations found in LI-COR (2011). Equation 1 for CH₄ fluxes differs from the CO₂-flux-density correction described by Eq. 24 in Webb et al. (1980) only through the addition of the A , B , and C coefficients that account for spectroscopic effects of water vapour, temperature, and pressure on CH₄ densities measured by the LI-7700 (McDermitt et al. 2011). At all sites, we used probe temperature measurements (HMP45 and HMP60; Viasala Inc., Vantaa, Finland) for \bar{T} in density corrections for CH₄ (Eq. 1), CO₂ (Eq. 24; Webb et al. 1980) and H₂O (Eq. 25; Webb et al. 1980) because absolute temperatures calculated from the sonic anemometers (WindMaster Pro, Gill Instruments, Hampshire, UK) can be offset from true temperature below 18 °C (Loescher et al. 2005).

We did not apply additional quality control to fluxes from the natural ecosystems with the exception of omitting extreme negative half-hourly fluxes (-100 nmol CH₄ m⁻² s⁻¹) from the alfalfa (0.1% of dataset; $n = 1$), pasture (no data removed), rice (1.6% of dataset, $n = 11$), and wetland (0.3%, $n = 2$). We used relaxed quality control criteria in order to compute daily

flux budgets without the necessity of gap filling within these short time series. Daily budgets were only computed for days with no data removed. Data quality was more variable in the airfield dataset, so we removed all fluxes with quality flags >7 according to stationarity tests from Foken and Wichura (1996). For CO₂ fluxes, we also removed fluxes from the airfield dataset with stationarity flags >7, and did not remove any CO₂ flux data from the ecosystem datasets. We only used airfield data collected when the wind direction sector was between 300° and 050°. Wind direction sectors from 035° to 155° were removed because an airplane hanger disturbed the flow from these wind directions, and wind directions from 155° to 300° were removed because the flux footprint extended to include non-pavement areas. Each night the wind direction would flip from the 000°–060° wind sector to the 155°–300° wind sector, and the flux footprint would elongate under stable conditions to include areas of grass and soil. The flux footprint for all remaining data from wind sectors 300° to 050° were collected from pavement only. All flux footprints used in the above analysis were calculated using an analytical two-dimensional footprint model (Detto et al. 2006; Hsieh et al. 2000). 78% of the remaining airfield CH₄ fluxes exhibited a high-degree of non-stationarity (>100%; flags 6–7 from Foken and Wichura (1996)) and were noisy; however, we needed to include these noisy data to have an adequate sample size to compare open- and closed-path fluxes. These CH₄ fluxes likely exhibited high degrees of non-stationarity due to changing wind directions as described above, and poor mixing conditions above the smooth asphalt surface. We did not compute daily budgets for the airfield dataset since our objective was to assess the influence of density corrections on flux budgets for natural ecosystems.

2.3 Cospectral Analysis

We evaluated the influence of heat- and water-vapour-induced density effects on observed turbulent CH₄ cospectra by comparing normalized cospectra of w and observed ρ_m to cospectra accounting for air-density-induced fluctuations to ρ_m . Comparing these cospectra is important because cospectra derived from observed molar densities alone may reflect effects of ρ_q or T fluctuations (Detto and Katul 2007) and may not represent true instrument performance or turbulent CH₄ fluxes. We can calculate ‘natural’ ρ_m (or $\rho_{m,nat}$) correcting for external water vapour and temperature fluctuations as a molar density following Detto and Katul (2007) and Detto et al. (2011) with the following equations,

$$\rho_{m,r} = \kappa(T, P_e)\rho_m \tag{2}$$

$$\rho'_{m,nat} = \rho'_{m,r} + \frac{\bar{\rho}_{m,r}}{\bar{\rho}_a} \rho'_q + \bar{\rho}_{m,r} \left(1 + \frac{\bar{\rho}_q}{\bar{\rho}_a} \right) \frac{T'}{T} \tag{3}$$

where $\rho_{m,r}$ is CH₄ density accounting for the spectroscopic effects of temperature and pressure using the dimensionless multiplier $\kappa(T, P_e)$ as described in McDermitt et al. (2011). This multiplier is identical to coefficient A in Eq. 1; however, instead of using half-hourly averaged data, we calculate $\kappa(T, P_e)$ in Eq. 2 using the parametric equations found in LICOR (2011) with 20-Hz temperature (T) and pressure data from the sonic anemometer and LI-7700, respectively. We then calculated cospectra for both ρ'_m and $\rho'_{m,nat}$ at alfalfa, pasture, wetland, and rice sites using only 30-min intervals measured during unstable conditions ($z/L < 0$), and for the negligible-flux sites, we normalized the $w'\rho'_{m,nat}$ cospectra by $w'\rho'_m$ because the density-corrected CH₄ flux ($w'\rho'_{m,nat}$) was near-zero at both sites. Normalizing (i.e. dividing) by zero renders the $w'\rho'_{m,nat}$ cospectra un-interpretable, so it is necessary to normalize by a shared flux of sufficient magnitude ($w'\rho'_m$). We did not present cospectra for the airfield because our primary interest was evaluating the influence of density fluctuations

on the interpretation of cospectra at field sites. All flux processing and cospectral analyses were conducted using in-house MATLAB software (Mathworks, Natick, Massachusetts, USA) (Detto et al. 2010; Hatala et al. 2012a; Knox et al. 2015), and data visualization and analyses were conducted using R 3.2.2 (Core Team 2015) and the ‘tidyverse’ package (Wickham 2016).

3 Results

3.1 Corrections over Zero-Flux and Negligible-Flux Ecosystems: Airfield, Alfalfa, and Pasture

Apparent CH_4 uptake that peaked around midday was observed in the uncorrected fluxes for the airfield test (Fig. 1a) and two negligible-flux sites (Fig. 1b,c). This peak coincided with the maximum daily sensible heat flux at all three sites (Fig. 1f–h). For the airfield test, outgoing energy fluxes were dominated by sensible heat, which peaked at 130 W m^{-2} in the afternoon (1430 LT) and no appreciable latent heat fluxes were observed (Fig. 1f). Thus, the water-vapour-flux term played no role in the density corrections and the entire correction

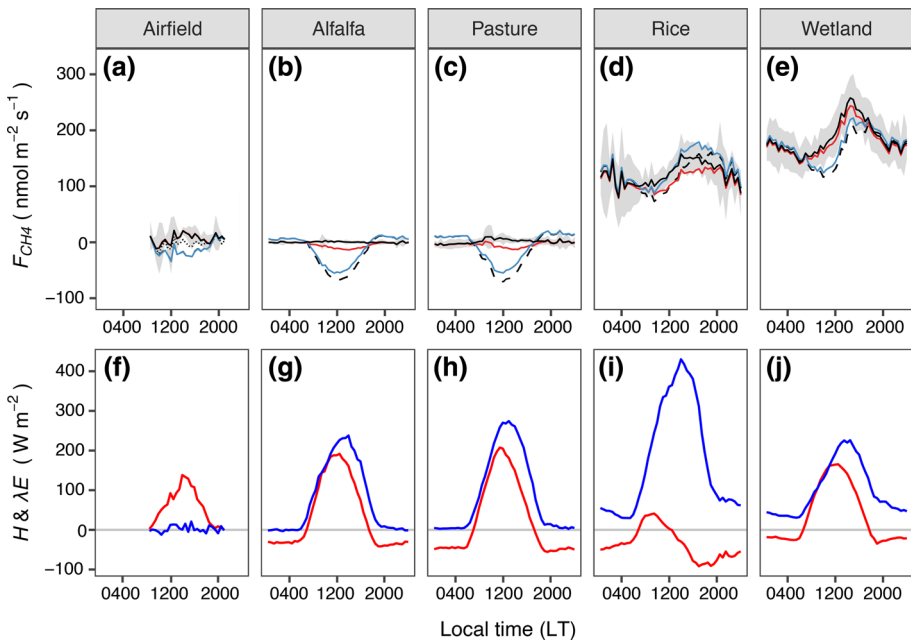
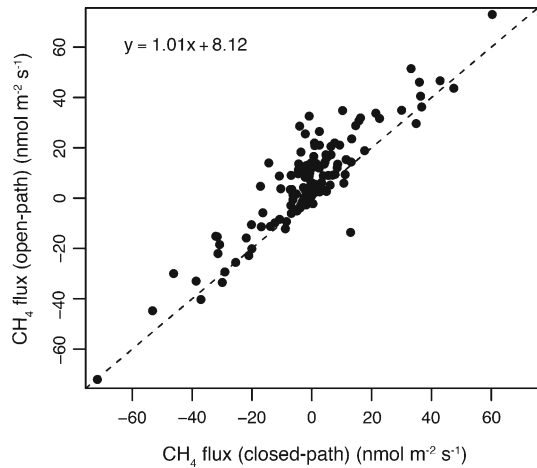


Fig. 1 Diel pattern in methane (F_{CH_4} ; top panel), sensible heat (H ; red line—bottom panel), and latent heat (λE ; blue line—bottom panel) fluxes for the airfield test and multiple ecosystems. Methane fluxes are shown for uncorrected (dashed line—top panel), water-vapour-only corrected (blue line—top panel), sensible-heat-only corrected (red line—top panel), and complete density-corrected CH_4 fluxes (black line—top panel). Grey shaded region on top panel bounds \pm one standard deviation of density-corrected CH_4 fluxes. Airfield test also includes CH_4 fluxes measured by the closed-path sensor (dotted line—top panel). For the airfield test, uncorrected and water-vapour-only corrected fluxes overlay one another as there was no latent heat flux from the airfield, and the sensible heat and complete density-corrected flux lines overlay one another because the entire correction arose from the sensible-heat-flux term

Fig. 2 Comparison of CH₄ fluxes measured by closed-path and open-path gas analyzers (density-corrected) above a pavement airfield. Dashed line represents the 1:1 line and inset regression statistics are for the orthogonal regression of open-path to closed-path fluxes



arose from the sensible-heat-flux term (Fig. 1a). Days were clear, mean wind speeds were 2.9 m s^{-1} (maximum of 7.6 m s^{-1}), and the 90% daytime flux footprint extended $\approx 330 \text{ m}$ and included areas of pavement airfield only. Airfield corrected fluxes were variable and near zero, though we observed significant positive CH₄ fluxes in the afternoon that can be interpreted as overcorrection to the density-corrected fluxes. These positive fluxes reached a peak of $23 \pm 12 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ ($\pm 95\%$ confidence interval) at 1600 LT when density corrections were largest (Fig. 1a). These fluxes cannot be viewed as noise given the zero detection limit of the system is $\approx 3.4 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ (Detto et al. 2011). Additionally, positive fluxes were not observed by the closed-path system during this mid-afternoon period (Fig. 1a). Closed-path fluxes were similarly variable and in generally good agreement with corrected open-path fluxes, with the exception of the positive bias observed in the open-path fluxes when closed-path fluxes were near zero (Fig. 2).

Fluxes from negligible-flux sites (alfalfa and pasture) follow similar patterns to the airfield, and apparent uptake by the land surface was corrected to a near-zero flux (Fig. 1b, c). The density correction produced a greater than 100% increase in computed daily CH₄ fluxes at both sites (Table 1). At these negligible-flux sites, fluctuations of ρ_m are low relative to absolute ρ_m in the atmosphere (Fig. 3). Most of the correction was driven by the sensible-heat-flux term (Fig. 1b, c), similar to the airfield study, even though latent and sensible heat fluxes were similar in magnitude over the course of the day for alfalfa and pasture (Fig. 1g, h).

Table 1 Daily CH₄ fluxes ($\text{mg CH}_4\text{-C m}^{-2} \text{ d}^{-1} \pm$ one standard deviation) for uncorrected ($F_{CH_4,O}$) and density-corrected CH₄ fluxes ($F_{CH_4,WPL}$), as well as percent change to daily fluxes due to density corrections ($\% \Delta F_{CH_4}$), percent of total density correction due to sensible heat ($\% H \Delta F_{CH_4}$), and the number of days (N) used to compute daily budgets

Site	$F_{CH_4,O}$	$F_{CH_4,WPL}$	$\% \Delta F_{CH_4}$	$\% H \Delta F_{CH_4}$	N
Alfalfa	-16 ± 3	0 ± 1	100	70	13
Pasture	-12 ± 5	1 ± 3	108	58	14
Rice	118 ± 9	121 ± 10	3	42	7
Wetland	175 ± 24	193 ± 24	10	64	13

To compute daily budgets we only used days with no data removal

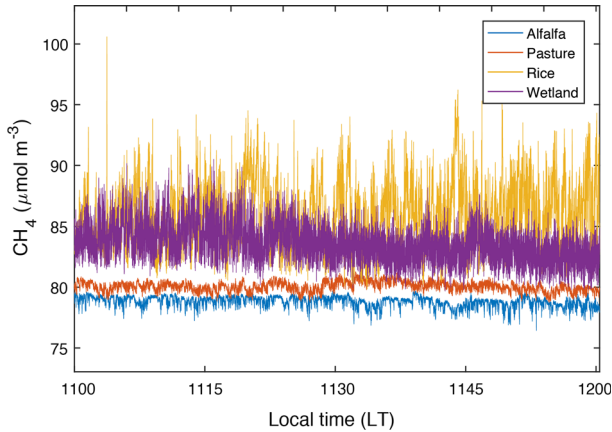


Fig. 3 Example high-frequency CH_4 densities for alfalfa, pasture, rice, and wetland sites from 1100 to 1200 LT on 17 August 2016

The sensible-heat-flux term was responsible for 70 and 58% of the total density correction for alfalfa and pasture, respectively (Table 1). At the alfalfa site, we observed a strong negative correlation between uncorrected CH_4 fluxes and sensible heat fluxes (Fig. 4, $r^2 = 0.98$). Corrected fluxes were zero ($0.1 \pm 0.2 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$; $\pm 95\%$ CI) across a range of H , with minor positive bias (Fig. 4; slope = 0.01, $P < 0.001$) that is undetectable by the open-path system for the range of sensible heat flux experienced at these sites. Comparing the cospectra of ρ_m and $\rho_{m,nat}$, we see a large spectral attenuation for $\rho_{m,nat}$ across most frequencies with the exception of the very high and low frequencies for both negligible-flux sites (Fig. 5a, b). This demonstrates that the ideal ρ_m cospectral response shown in Fig. 5a,

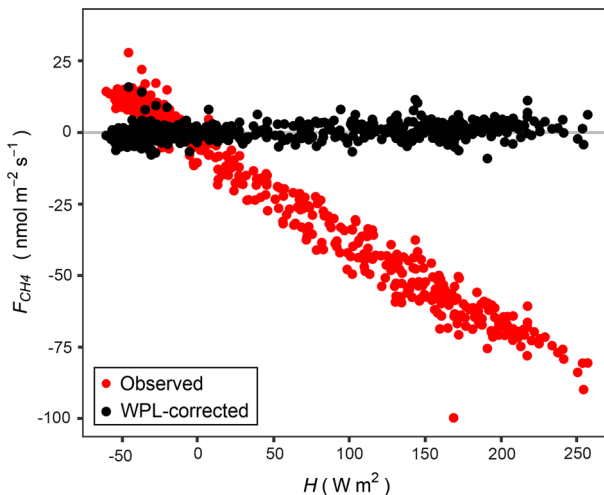


Fig. 4 Relationship of CH_4 fluxes (F_{CH_4}) and sensible heat flux (H) for uncorrected (red points) and density-corrected CH_4 fluxes (black points) over a drained alfalfa field. Corrected fluxes were not significantly different from zero ($0.1 \pm 0.2 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$; $\pm 95\%$ confidence interval)

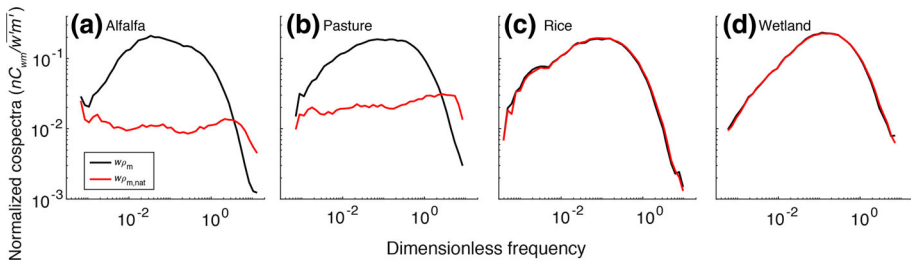


Fig. 5 Normalized cospectra of observed (ρ_m) and natural ($\rho_{m,nat}$) CH_4 density for alfalfa (a), pasture (b), rice (c), and wetland (d) sites. Only data collected during unstable conditions ($z/L < 0$) were used in the analysis. For panels (c) and (d) the ρ_m cospectra (black line) sits directly behind the $\rho_{m,nat}$ cospectra (red line), as values were nearly identical. The dimensionless frequency $f = nz/U$.

b (black lines) is an artifact of T and ρ_q fluctuations and does not reflect the true CH_4 flux cospectra at these sites.

3.2 Corrections over High-Flux Ecosystems: Rice and Restored Wetland

For the high-flux sites, density corrections primarily adjusted the diel pattern in CH_4 fluxes, as the impact to daily budgets was low, causing a 3 and 10% adjustment in daily budgets for rice and restored wetland, respectively (Table 1). Smaller corrections occur at these high-flux sites because the fluctuations of ρ_m are much larger relative to absolute ρ_m in comparison to the negligible-flux sites (Fig. 3). For rice, the density correction shifted the CH_4 flux diel peak to earlier in the day, from 1900 to 1630 LT, but did not alter the peak magnitude (Fig. 1d). The rice site was the only site where the sensible-heat-flux correction was smaller than the water-vapour correction (42% sensible heat term; Table 1). Latent heat fluxes were much larger than sensible heat fluxes from rice (Fig. 1i), and the water-vapour-flux and sensible-heat-flux correction terms often exerted a similar magnitude and opposite sign influence on the total correction (Fig. 1d). For the wetland, the density correction increased the magnitude of the afternoon CH_4 flux peak but did not shift the timing (Fig. 1e), and the daily minimum flux was shifted from midday to morning after applying corrections (Fig. 1e). Unlike rice, 64% of the flux correction is due to the sensible-heat-flux correction term (Fig. 1e; Table 1). Positive sensible heat fluxes were observed from the wetland throughout the day (Fig. 1j) when rice sensible heat fluxes were often zero or negative (Fig. 1i), and wetland sensible heat and latent heat fluxes were more balanced, similar to pasture and alfalfa (Fig. 1g, h). No spectral attenuation was visible for $\rho_{m,nat}$ across all frequencies for the rice and wetland sites (Fig. 5c, d), demonstrating that the observed ρ_m cospectra is a true reflection of CH_4 fluxes rather than an artifact of T and ρ_q induced fluctuations.

4 Discussion and Conclusions

Our results demonstrate that density corrections applied to fluxes measured with open-path infrared spectrometers (Webb et al. 1980) play an important role in accurately determining diel patterns and daily budgets for CH_4 fluxes. Application of density corrections are susceptible to errors in the measurement of sensible and latent heat fluxes, which could therefore lead to biases when computing CH_4 budgets as well as identifying biophysical drivers of CH_4 fluxes. Density corrections shifted the diel flux pattern in both rice and wetland ecosystems, and these

shifts could be a concern to studies identifying relationships and lags between biophysical drivers and CH₄ fluxes, such as those using time-series cross-correlation or spectral analyses (Hatala et al. 2012b; Chamberlain et al. 2016; Sturtevant et al. 2016). Concerns related to computing reliable budgets are most relevant in low-flux ecosystems, where we observed that the application of density corrections led to in excess of a 100% change to daily CH₄ budgets. The impact of the density correction on daily budgets was considerably less over wet ecosystems with sustained positive fluxes. Potential errors in density corrections are therefore less important, but still relevant, when computing budgets for high-flux sites where open-path CH₄ sensors are more likely to be deployed. Our findings have relevance to the future development of open-path sensors for additional trace gases, such as nitrous oxide (N₂O). Ecosystem N₂O fluxes are often characterized by ‘hot moments’, where pulse emissions are followed by extended zero-flux periods (Jones et al. 2011). In such cases, the application of accurate density corrections will be of central importance, as large biases could arise during extended zero-flux periods when the corrections play a more important role in adjusting daily flux budgets.

We found that the density correction successfully re-zeroed CH₄ fluxes over negligible-flux ecosystems, such as alfalfa and pasture, and previous chamber and tower-based research demonstrates that similar ecosystems have near-zero fluxes during dry periods (Teh et al. 2011; Chamberlain et al. 2015, 2016, 2017). Data collected from our airfield experiment were noisier and near zero; however, small positive fluxes were calculated post-correction with a maximum false positive flux of $23 \pm 12 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ ($\pm 95\%$ confidence interval; $n = 3$). These positive fluxes are likely an error rather than a true flux because maximum observed CH₄ emissions from pavement asphalt are on the order of $0.4 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ (Tyler et al. 1990), which is below the detection limit of open-path CH₄ eddy-covariance systems (Detto et al. 2011). Kondo and Tsukamoto (2008) observed similar false positive CO₂ fluxes during a pavement experiment, where the bias was attributed to overcorrection in the sensible-heat-flux term of the density correction. This observation was driven by differences in spectral performance between instruments used to measure CO₂ (open-path gas analyzer) and sensible heat (sonic anemometer) fluxes. Here, high-frequency losses were observed for CO₂ fluxes, but not sensible heat fluxes, causing an overcorrection by the density correction due to the sensible-heat-flux term (Kondo and Tsukamoto 2008). However, these errors can be minimized by applying high-frequency loss corrections to observed CO₂ fluxes prior to implementing density corrections (Foken et al. 2012).

Notably, we did not observe any detectable positive bias to density-corrected fluxes measured from drained alfalfa (Fig. 4), suggesting that the observed airfield correction errors are site or instrument specific. We can infer that the observed zero flux is not an overcorrection of CH₄ uptake by soils because reported CH₄ uptake rates by grasslands and croplands are as high as $0.84 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ (Hütsch 2001), which is well below the detection limit of open-path CH₄ eddy covariance (Detto et al. 2011). These site-to-site differences in correction error demonstrate that bias due to sensor performance may affect CH₄ budgets in some cases only, and care should be taken to evaluate the performance of corrections and instruments across sites. Overcorrection is likely relevant at low-flux sites, as we observe mean fluxes of $0.1 \pm 1.1 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ and $1.3 \pm 3.9 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ for alfalfa and pasture, respectively, and the maximum bias observed at the airfield was over 17 times the mean flux in either ecosystem. In contrast, the impact of overcorrection should be much smaller for high-flux sites because observed airfield errors were $\approx 20 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ for a few hours in the afternoon, whereas daily average fluxes from the rice and wetland were $122 \pm 20.0 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ and $186 \pm 30.0 \text{ nmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$, respectively. Overcorrection arising from the sensible-heat-flux term is still likely relevant to a wide-range of

ecosystems, as we observed that sensible heat flux was responsible for most of the density correction across a range of wet and dry sites (Table 1). Even in the case of rice, where latent heat flux was clearly dominant and sensible heat fluxes were near zero (Fig. 1i), the sensible-heat-flux term was responsible for over 40% of the total correction. These findings suggest that biases affecting sensible-heat-flux corrections should not be ignored, even for ecosystems where energy fluxes are dominated by latent heat. High-frequency spectral corrections for CH₄ fluxes should therefore be considered before applying density corrections to reduce this source of error (Foken et al. 2012).

Care should also be taken when interpreting the spectral performance of CH₄ sensors across low-flux and high-flux sites, and high frequency data from low-flux sites should be transformed to $\rho_{m,nat}$ before assessing the cospectral density of w' and ρ'_m . We demonstrate that for negligible-flux sites the CH₄ flux cospectra are significantly attenuated across a wide range of frequencies when controlling for external air-density fluctuations, where the cospectral responses for ρ_m are artifacts of T and ρ_q fluctuations (Fig. 5a, b). Investigators should therefore be cautious using measured CH₄ densities to infer information about turbulent flux characteristics for low-flux ecosystems, and it is important to correct for these effects as in Detto and Katul (2007) and applied in Detto et al. (2011). However, correcting for external density fluctuations led to no observable change in cospectral density at high-flux sites, showing that the application of density corrections to high-frequency data for cospectral analysis should be applied on a site-by-site basis, but is required to properly assess CH₄ flux cospectra in low- or intermittent-flux ecosystems.

Our results demonstrate that density corrections to CH₄ fluxes play a similarly important role in accurately determining flux budgets and diel patterns as previously described for CO₂ fluxes (Leuning et al. 1982; Ham and Heilman 2003; Kondo and Tsukamoto 2008). Past work over natural systems has shown that density corrections to CO₂ fluxes are responsible for the largest magnitude flux correction (Foken et al. 2012), and these adjustments can account for a 20–80% change in daily budgets (Ham and Heilman 2003). Our work shows a similar, and often larger, role in the adjustment of daily CH₄ fluxes (Table 1), and overall we compute a similar range in percentage changes to daily CH₄ fluxes (range 3–108%) and daily CO₂ fluxes (range 3–111%; data not shown). Overall, we demonstrate that density corrections play an important role in accurately determining ecosystem CH₄ fluxes, and careful application and evaluation of density corrections are needed as more CH₄ flux monitoring sites come online. The dominant influence of density corrections on data interpretation also varies widely between high- and low-flux ecosystems, and the corrections primarily influence the evaluation diel patterns for high-flux ecosystems. The impact of density corrections on flux budgets is more pronounced over low- or intermittent-flux ecosystems, which has broad relevance to the application and development of open-path sensors for additional trace gas species.

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