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ORIGINAL PAPER

Consequences of Uncertainties in CO_2 Density for Estimating Net Ecosystem CO_2 Exchange by Open-path Eddy Covariance

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Abstract Errors in the estimation of CO_2 surface exchange by open-path eddy covariance, introduced during the removal of density terms [Webb et al. Quart J Roy Meteorol Soc 106:85–100, (1980) - WPL], can happen both because of errors in energy fluxes [Liu et al. Boundary-Layer Meteorol 120:65–85, (2006)] but also because of inaccuracies in other terms included in the density corrections, most notably due to measurements of absolute CO_2 density (ρ_c). Equations are derived to examine the propagation of all errors through the WPL algorithm. For an open-path eddy covariance system operating in the *Sierra de Gádor* in south-east Spain, examples are presented of the inability of an unattended, open-path infrared gas analyzer (IRGA) to reliably report ρ_c and the need for additional instrumentation to determine calibration corrections. A sensitivity analysis shows that relatively large and systematic errors in net ecosystem exchange (NEE) can result from uncertainties in ρ_c in a semi-arid climate with large sensible heat fluxes (H_s) and (wet) mineral deposition. When ρ_c is underestimated by 5% due to lens contamination, this implies a 13% overestimation of monthly CO_2 uptake.

Keywords Density correction · Eddy covariance · Error propagation · Open-path infrared gas analyzer

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1 Introduction

Infrared gas analyzers (IRGAs) of open-path design, measuring CO_2 and water vapour density (ρ_c and ρ_v, respectively) rather than mixing ratio (c and s accordingly) are now used routinely in eddy covariance studies of net ecosystem exchange (NEE), requiring systematic "corrections" for density effects (Webb et al. 1980) (hereafter, WPL terms). Because the WPL terms represent significant differences between the open-path eddy covariance and the CO_2 flux (F_C), their accuracy can determine the uncertainty in F_C. Due to the importance and magnitude of these WPL terms, particularly in semi-arid climates where large sensible heat fluxes (H_s) are typical (midday $H_s > 250\,\mathrm{W\,m^{-2}}$), the influence of energy balance measurement errors on the uncertainty in open-path F_C has been previously assessed (Liu et al. 2006).

However, uncertainties in WPL terms are due not only to errors in energy fluxes but also to inaccurate measurements of ρ_c, ρ_v, air temperature (T) and atmospheric pressure (p). In the case of ρ_c, previous studies have warned against the potential for degraded performance of unattended open-path instruments due to the contamination of optical surfaces by the elements (Leuning and Judd 1996; Leuning and Moncrieff 1990). This contamination causes underestimation of ρ_c and a selective, systematic error (Moncrieff et al. 1996) in NEE, via the WPL terms.

Here we extend the Liu et al. (2006) analysis to include all scalars whose errors affect the WPL corrections. To characterize the most important errors, we present errors in open-path ρ_c measurements, as systematic underestimation due to contamination of the optical windows, and demonstrate the possibility of solving the problem with additional ρ_c or ρ_v measurements. The resulting errors in NEE are presented in such a way as to complete the assessment (Liu et al. 2006) of the propagation of errors through the WPL terms. Finally, we examine the bias in monthly NEE estimates at a semi-arid montane shrubland ecosystem due to the selective, systematic error (diurnal bias) introduced into F_C due to the underestimation of ρ_c via the WPL terms.

2 Theoretical Considerations

The turbulent CO_2 flux (F_C) can be accurately determined by eddy covariance using open-path IRGAs to quantify vertical wind and CO_2 density fluctuations (covariance), and applying the WPL terms to account for the density effects. Here, we directly adapt Eq. 24 of Webb et al. (1980), factoring a common ρ_c out of the final two terms:

$$F_C = \overline{w'\rho_c'} + \overline{\rho_c}\left[\frac{\mu\overline{w'\rho_v'}}{\overline{\rho_a}} + \frac{(1+\mu\overline{\rho_v}/\overline{\rho_a})\overline{w'T'}}{\overline{T}}\right], \tag{1}$$

where w is the vertical wind, ρ is the gas density, T is the air temperature, and $\mu = m_a/m_v$; m is the molecular mass; subscripts a, v, and c refer respectively to dry air, water vapour, and CO_2. Following micrometeorological convention, overbars denote mean quantities and turbulent-scale fluctuations are marked by primes. In our analyses, air density ($\overline{\rho_a}$) is substituted by $\overline{p}/R_a\overline{T}$ according to the gas law. One can hardly overstate the importance of Eq. 1 for open-path eddy covariance, since the magnitude of the "correction" can exceed the resulting flux (Leuning et al. 2005).

Differentiating Eq. 1 not only with respect to the three covariance terms (Liu et al. 2006) but also with respect to scalars (ρ_c, ρ_v, T, and p) and expressing the results in terms of ($\overline{\rho_a}$), instead of $\overline{p}$, R, and $\overline{T}$, we obtain:

$$
\begin{aligned}
\frac{\delta F_C}{F_C} = {} & \underbrace{\left[\frac{\overline{w'\rho'_c}}{F_C}\right]}_{C_1} \frac{\delta\overline{w'\rho'_c}}{\overline{w'\rho'_c}} + \underbrace{\left[\frac{\mu\overline{w'\rho'_v}}{F_C}\frac{\overline{\rho_c}}{\overline{\rho_a}}\right]}_{C_2} \frac{\delta\overline{w'\rho'_v}}{\overline{w'\rho'_v}} + \underbrace{\left[\frac{\overline{\rho_c}\,\overline{w'T'}}{\overline{T}F_C}\left(1+\mu\frac{\overline{\rho_v}}{\overline{\rho_a}}\right)\right]}_{C_3} \frac{\delta\overline{w'T'}}{\overline{w'T'}} \\
& + \underbrace{\left[\frac{\mu\overline{w'\rho'_v}}{F_C}\frac{\overline{\rho_c}}{\overline{\rho_a}} + \left[\frac{\overline{\rho_c}\,\overline{w'T'}}{\overline{T}F_C}\left(1+\mu\frac{\overline{\rho_v}}{\overline{\rho_a}}\right)\right]\right]}_{C_4} \frac{\delta\overline{\rho_c}}{\overline{\rho_c}} \\
& + \underbrace{\left[\frac{\overline{\rho_c}\,\overline{w'T'}}{\overline{T}F_C}\left(\mu\frac{\overline{\rho_v}}{\overline{\rho_a}}\right)\right]}_{C_5} \frac{\delta\overline{\rho_v}}{\overline{\rho_v}} + \underbrace{\left[\frac{\mu\overline{w'\rho'_v}\,\overline{\rho_c}}{\overline{\rho_a}F_C} - \frac{\overline{w'T'}\,\overline{\rho_c}}{\overline{T}F_C}\right]}_{C_6} \frac{\delta\overline{T}}{\overline{T}} \\
& + \underbrace{\left[-\frac{\mu\overline{w'\rho'_v}\,\overline{\rho_c}}{\overline{\rho_a}F_C} - \left[\frac{\overline{\rho_c}\,\overline{w'T'}}{\overline{T}F_C}\left(\mu\frac{\overline{\rho_v}}{\overline{\rho_a}}\right)\right]\right]}_{C_7} \frac{\delta\overline{p}}{\overline{p}}.
\end{aligned}
\tag{2}
$$

Following the Liu et al. (2006) notation, we see that perturbations in calculated CO_2 fluxes ($\delta F_C/F_C$) are related not only to changes in the raw CO_2 covariance ($\varpi_c = \delta\overline{w'\rho'_c}/\overline{w'\rho'_c}$), and errors in kinematic sensible heat flux and water vapour covariance ($\varpi_T = \delta\overline{w'T'}/\overline{w'T'}$, $\varpi_v = \delta\overline{w'\rho'_v}/\overline{w'\rho'_v}$) but also to changes in CO_2 density ($\varpi_{\rho_c} = \delta\overline{\rho_c}/\overline{\rho_c}$), water vapour density ($\varpi_{\rho_v} = \delta\overline{\rho_v}/\overline{\rho_v}$), air temperature ($\varpi_{\overline{T_a}} = \delta\overline{T}/\overline{T}$) and air pressure ($\varpi_p = \delta\overline{p}/\overline{p}$). The magnitude of these errors will depend on their corresponding coefficients [C_1, C_2, C_3, C_4, C_5 C_6, and C_7, respectively; Eq. 2] that vary with time and atmospheric conditions (Liu et al. 2006). The cited authors applied Eq. 2, neglecting errors in scalar terms, to identify the potential magnitudes of raw systematic errors for open-path eddy covariance systems associated with the evaluation of energy balance closure (ω_c, ω_v, and ω_T) (Liu et al. 2006 (Sect. 4.1)). Here, we add to the Liu et al. (2006) analysis the effects of errors in ρ_v, T and p and demonstrate that they are negligible. We also present the consequences of underestimating ρ_c due to contamination of open-path window lenses (as propagated through the WPL terms).

3 Field Site and Measurements

The primary data examined here to quantify errors in ρ_c measurements and their implications in NEE are from an open-path IRGA (LI-7500, LI-COR, Lincoln, NE, USA), which reported ρ_c, ρ_v, and p; and from a three-axis sonic anemometer (CSAT-3, Campbell Scientific, Logan, UT, USA), which reported wind speed and sonic temperature; both instruments are located at 2.5 m above the surface. A data-logger (CR23X, CSI) managed the measurements and recorded the data, with means, variances, and covariances of 10 Hz data calculated and stored every 15 min.

The analyses presented below depend on additional measurements of atmospheric and soil state. A thermohygrometer (HMP 35C, CSI, USA) at 1.5 m above the surface measured air temperature and humidity (accuracy of ±0.1% and ±2% respectively at 293.15°C), and was used in combination with the gas law to provide independent estimates of ρ_v. A tipping bucket (0.2 mm) raingauge (model 785 M, Davis Instruments Corp., Hayward, CA, USA) quantified rainfall and three leaf wetness sensors (237-LC, Campbell Scientific inc. UK) detected dew and rainfall events. A quantum sensor (Li-190, Li-Cor, Lincoln, NE, USA) deployed at 1.5 m height measured incident fluxes of photons in photosynthetic wavelengths. Finally, soil temperature was determined as the mean of four thermocouples (TCAV, CSI) at 10, 20, 40, and 80 mm depth. The latter two measurements were used to fill daytime and nighttime data gaps (Falge et al. 2001) for integration to long term fluxes.

The measurements were made in a sub-alpine shrubland ecosystem in the *Sierra de Gádor* in south-east Spain: for more information see Serrano-Ortiz et al. (2007).

4 Results and Discussion

4.1 Errors in ρ_c Measurements using Open-path IRGAs Due to Lens Contamination

We present [CO_2] (the molar fraction in units of ppm) because it is unaffected by temperature fluctuations; in terms of the relative IRGA errors observed, [CO_2] and ρ_c are equivalent. Figure 1 shows 10 weeks of mean [CO_2] from the shrubland ecosystem around the end of summer, 2005. On three dates (circled), the windows were cleaned and its zero and span compared very well with standard references of pure (99.999%) nitrogen and 479 ± 2 ppm CO_2, such that no calibration corrections were required.

Rain causes false readings due to infrared extinction by liquid water, but also leads to lasting step changes in reported [CO_2] seen as relative errors often well in excess of 5%. In the worst incidence observed here, a 21 July cleaning corrected a 15% underestimation. Rain dramatically changes the purity of the windows at this site, usually by soiling them and leading to underreporting of ρ_c. One rain episode on 7 September apparently had a net rinsing effect on the windows, but still left them unclean. This region of south-east Spain, where *la lluvia de barro* (dirty rain) is well-known (Queralt- Mitjans et al. 1993), may represent an extreme situation regarding lens contamination. However, since dirty rain is common at other Mediterranean sites (Penzar and Poje 1999–2000) and farther afield (Great Plains, U.S.A.; Editors 1899), the problem is not purely local. What is more, these results show clearly that instrument performance determined at two points in time may not represent the intervening period, and rain frequently induces errors exceeding several percent in [CO_2].

Correcting the underestimation of ρ_c after rain is not viable by post-calibration, but requires additional information. To be of use in this context, calibration checks must occur more frequently than do changes in optical cleanliness, an impossibility for unattended monitoring. Additionally, the standard calibration tube (Li-Cor 2002) cannot physically be inserted

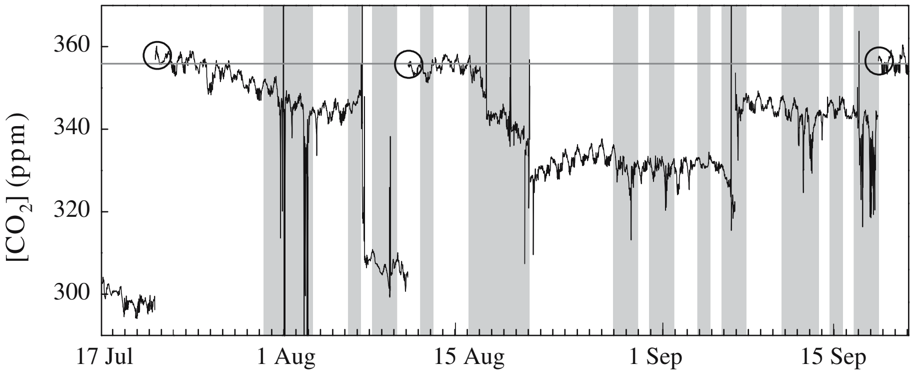

Fig. 1 Carbon dioxide molar fraction [CO_2] determined during late summer 2005 at the *Sierra de Gádor* field site. Days with rain are shaded. Open circles indicate periods where the windows of the IRGA were cleaned and its response checked against standard gas reference values

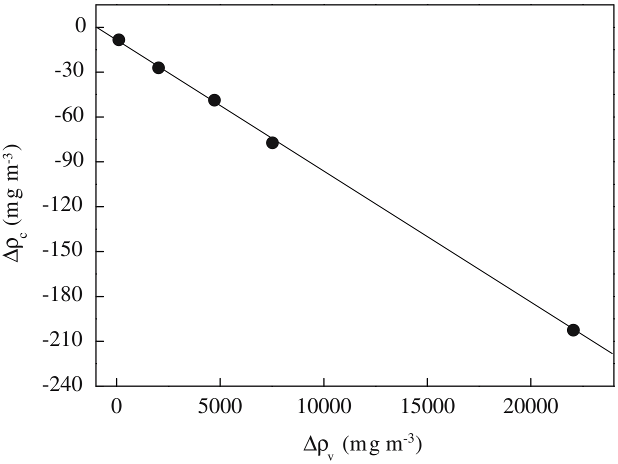

Fig. 2 Errors in CO_2 density are strongly correlated (N = 5; $R^2 = 0.9998$) with those for water vapour due to optical lens contamination. The CO_2 density error ($\Delta\rho_c$) is the difference before and after cleaning the IRGA optical windows. The water vapour density difference ($\Delta\rho_v$) compares the dirty case with an independent themohygrometer

into the sensor head without rubbing/wiping at least one of the optical windows. Unfortunately, the diagnostic parameter for window purity (AGC) reported by the instrument during serial data logging (SDM) lacks sufficient resolution to detect some of the 5% step changes mentioned above. Therefore, reliable and independent information regarding either ρ_c or ρ_v is needed in order to correct mean density errors reported by such open path IRGAs.

In Fig. 2, we present absolute errors in ρ_c corrected by window cleaning (five lens cleaning episodes) versus errors in ρ_v using the thermohygrometer as a reference. The strong relationship between lens contamination errors for CO_2 and water vapour represents a means of correcting for such errors, where an independent instrument such as the HMP 35C is used to estimate the water vapour density. Such empirical corrections, like the lens contaminants from which they derive, are likely site-specific.

The concurrent over-estimation of ρ_v and under-estimation of ρ_c (negative slope in Fig. 2) are consistent with the LI-7500 operating principle and the infrared properties of likely contaminants such as mineral dust. This IRGA model estimates ρ_c as inversely proportional to the transmittance ratio (R_τ, at the detector) of power in the CO_2 absorbing wavelength (4.25 μm) divided by that for a reference wavelength (3.95 μm). Although selected to avoid gas absorptance, the reference wavelength is nevertheless susceptible to the effects of lens contaminants. Since infrared transmission by mineral dust increases with increasing wavelength (Collaud Coud et al. 2004; Lyamani et al. 2006), lens contamination more strongly affects the numerator, increasing R_τ and thus leading to an underestimation of ρ_c. Conversely for water vapour, R_τ is defined with a shorter gas-absorbing wavelength (2.59 μm) in the numerator (and the same reference denominator), and so is decreased by dust, causing an over-estimation of ρ_v.

Importantly, neither the variance of ρ_c nor its covariance with vertical winds exhibited step changes (such as in Fig. 1) associated with changes in window cleanliness (not shown). Apparently, lens contamination affects only the zero and not the span of the IRGA.

4.2 Implications for Relative Errors in CO_2 Flux: Completing the Liu et al. (2006) analysis

We divide the effects of propagating errors in the CO_2 flux into two sections. First, we present relative errors in the CO_2 flux due to measurement errors in scalars (ρ_v, T, and p), which are shown to be negligible. A second section presents errors of greater significance, grouping those due to systematic errors in the kinematic sensible heat flux and the raw covariances for water vapour and CO_2 (following Liu et al. 2006) together with those associated with underestimation of ρ_c for unclean open-path optical windows.

4.2.1 Scalar Measurement Errors Contributing to Negligible Errors in the CO_2 Flux

In this section we estimate errors in ρ_v, T, and p measurements (ϖ_{ρ_v}, $\varpi_{\overline{T}_a}$, and ϖ_p; Eq. 2) and demonstrate that the magnitude of these errors (that depend on their respective corresponding coefficients C_5, C_6 and C_7; Equation 2) can be neglected.

Our analysis assumes that errors associated with ρ_v, T, and p depend on the accuracy of the direct measurements from which they derive. The thermohygrometer measures relative humidity (U) and T, respectively (over appropriate ranges) with relative accuracies of $\varpi_U = \pm 2\%$ and $\varpi_{\overline{T}_a} = \pm 0.1\%$, while the open-path IRGA measures p to within $\varpi_p = \pm 1.5\%$. We estimate ρ_v from thermohygrometric data via the equation of state for water vapour ($\overline{\rho_v} = e/(R_v\overline{T})$, where e is the water vapour pressure and R_v the gas constant), and the definition of U ($e = e_s U$, where e_s is the saturation water vapour pressure), such that:

$$\varpi_{\rho_v} = \frac{\delta\overline{\rho_v}}{\overline{\rho_v}} = \frac{de}{e} + \frac{dT}{\overline{T}} = \frac{dU}{\overline{U}} + \frac{de_s}{e_s} + \frac{dT}{\overline{T}}. \tag{3}$$

Using the Clausius–Clapeyron equation (and neglecting the slight temperature dependence of latent heat) to describe the dependence of e_s on T, we obtain:

$$\varpi_{\rho_v} = \frac{dU}{\overline{U}} + \frac{L_v dT}{R_v\overline{T}^2} + \frac{dT}{\overline{T}} = \varpi_U + \left(\frac{L_v}{R_v\overline{T}} + 1\right)\varpi_{\overline{T}_a}, \tag{4}$$

where L_v is the latent heat of vaporisation. The value in parenthesis is of order 20, so that ϖ_{ρ_v} cannot exceed ±5%, but note, however, that if ρ_v is taking from open-path IRGA measurements (not recommended here), lens contamination can cause ϖ_{ρ_v} to exceed +50% following dirty rain.

In any event, the contribution of these errors ($\varpi_{\rho_v} \simeq \pm 5\%$, $\varpi_{\overline{T}_a} \simeq \pm 0.1\%$, and $\varpi_p \simeq \pm 1.5\%$) to the relative errors in the CO_2 flux can be neglected compared to both the systematic errors assumed in the Liu et al. (2006) analysis and those presented in the following section. Even for the largest values, where relative errors in ρ_v and p exceed ±1%, the low values of their corresponding coefficients ensure negligible contribution to the relative error in the CO_2 flux. For example, C_5 is two orders of magnitude smaller than C_3 (the coefficient for the kinematic sensible heat flux error; Liu et al. (2006)), negating the importance of the ±5% relative error in ρ_v. Likewise, the ±1.5% value for ϖ_p (one tenth that of ϖ_T) is multiplied by C_7, defined as the sum (with opposite signs) of C_5 (small) and the coefficient C_2, which is quite small compared to C_3. To summarize, the contributions to the relative error in the CO_2 flux due to errors in these scalars are negligible.

4.2.2 Relative Errors in the CO_2 Flux Due to a Systematic Underestimation of ρ_c

To evaluate the effects of propagating errors in ρ_c, we follow the analysis in Sect. 4.2.1 of Liu et al. (2006), who, in the present context, consider an assumption that sensible and latent heat fluxes are underestimated by about 15% during daytime and by about 30% at night, and also assume that raw CO_2 fluxes are 15% too low. In complementing the analyses of Liu et al. (2006) and generating Tables 1 and 2, we repeat their assumptions and consider five cases: no errors in ρ_c for clean open-path optical windows (Case Ia) and relative errors in ρ_c of −2%, −5%, −10% and −25% due to dirty lenses (Cases Ib, Ic, Id, and Ie, respectively). Our Table 1 shows that while errors in the energy balance closure (Case Ia) can induce relative errors in F_C from 13% to 27% (depending on the magnitude of H_s), just a 5% underestimation of ρ_c (Case Ic) can increase relative errors in F_C up to maximum of 65%.

As seen in the Liu et al. (2006) analyses, the effects of propagating errors via WPL terms depend strongly on H_s. In addition, it is important to note that the H_s dependence for the ρ_c coefficient (C_4), which determines the magnitude of the F_C error associated with errors in

Table 1 Error estimates of daytime CO_2 fluxes

Sensible heat flux ($W\,m^{-2}$)	Coefficients in Equation (1)				$\delta F_C / F_C$ in Equation (1) (%)				
	C_1	C_2	C_3	C_4	Case Ia*	Case Ib*	Case Ic*	Case Id*	Case Ie*
50	1.76	−0.15	−0.77	−0.93	−12.8	−10.7	−8.0	−3.3	+10.7
100	2.15	−0.19	−1.20	−1.39	−11.5	−8.6	−4.5	+2.5	+23.4
150	2.64	−0.23	−1.88	−2.03	−8.0	−3.9	+2.2	+12.4	+42.8
200	3.23	−0.27	−2.80	−3.07	−2.3	+3.7	+13.0	+28.3	+74.4
250	3.91	−0.30	−3.99	−4.29	+5.5	+14.3	+27.2	+48.6	+113.0
300	4.71	−0.33	−5.42	−5.75	+15.6	+27.1	+44.4	+73.1	+159.4
350	5.60	−0.35	−7.10	−7.45	+27.7	+42.7	+65.0	+102.3	+214.0

$^*\frac{\delta\overline{w'\rho_c'}}{\overline{w'\rho_c'}} = -15\%\quad \frac{\delta\overline{w'\rho_v'}}{\overline{w'\rho_v'}} = -15\%\quad \frac{\delta\overline{w'T'}}{\overline{w'T'}} = -15\%;$

1a, $\frac{\delta\overline{\rho_c}}{\rho_c} = 0\%$; 1b, $\frac{\delta\overline{\rho_c}}{\rho_c} = -2\%$; 1c, $\frac{\delta\overline{\rho_c}}{\rho_c} = -5\%$; 1d, $\frac{\delta\overline{\rho_c}}{\rho_c} = -10\%$; 1e, $\frac{\delta\overline{\rho_c}}{\rho_c} = -25\%$

Table 2 Error estimates of nighttime CO_2 fluxes

Sensible heat flux ($W\,m^{-2}$)	Coefficients in Equation (1)				$\delta F_C / F_C$ in Equation (1) (%)				
	C_1	C_2	C_3	C_4	Case Ia*	Case Ib*	Case Ic*	Case Id*	Case Ie*
−25	1.45	0.04	−0.97	−0.95	−15.9	−13.7	−10.9	−6.1	8.2
−50	1.75	0.06	−1.17	−1.11	−19.0	−17.0	−13.7	−8.1	8.6
−75	2.12	0.08	−1.46	−1.38	−22.2	−19.4	−15.3	−8.4	12.3
−100	2.59	0.09	−1.83	−1.74	−25.5	−22.0	−16.8	−8.1	18.0

$^*\frac{\delta\overline{w'\rho_c'}}{\overline{w'\rho_c'}} = -30\%\quad \frac{\delta\overline{w'\rho_v'}}{\overline{w'\rho_v'}} = -30\%\quad \frac{\delta\overline{w'T'}}{\overline{w'T'}} = -15\%;$

1a, $\frac{\delta\overline{\rho_c}}{\rho_c} = 0\%$; 1b, $\frac{\delta\overline{\rho_c}}{\rho_c} = -2\%$; 1c, $\frac{\delta\overline{\rho_c}}{\rho_c} = -5\%$; 1d, $\frac{\delta\overline{\rho_c}}{\rho_c} = -10\%$; 1e, $\frac{\delta\overline{\rho_c}}{\rho_c} = -25\%$

ρ_c, is stronger than for the other coefficients because C_4 can be expressed as the sum of C_2 and C_3. Therefore, high values of H_s in combination with higher relative errors in ρ_c imply even larger errors in F_C via WLP terms than is the case for the energy flux errors. In any event, the relative uncertainty in F_C due to errors in ρ_c is similar in magnitude to that caused by errors in the energy balance.

Due to this H_s dependence, the WPL terms generally have far greater magnitudes during daytime than at night (Miller et al. 2004; Paw U et al. 2000). This diurnal weighting implies that systematic errors in the WPL terms lead to *selectively* systematic errors in F_C (Moncrieff et al. 1996), likely the most severe type of error in long-term integrations of NEE.

4.3 Implications of a Systematic ρ_c Underestimation for the Determination of NEE

In this section we assume no errors in F_C due to other factors ($\omega_c = \omega_v = \omega_T = 0$) and analyze the implications of a 5% underestimation of ρ_c on integrated NEE estimates from a semi-arid montane shrubland ecosystem. The data presented are from June 2004, a period when lens cleanliness was assured, yet in a season when episodes of *lluvia de barro* are frequent in south-east Spain. Figure 3 compares the mean diurnal trend in F_C with that effected by a 5% underestimation of ρ_c. It is clear that the diurnal bias implies a selectively systematic error in the estimated NEE, as daytime uptake is overestimated far more than nighttime release. The monthly integration is $-0.041\,\mathrm{kg\,C\,m^{-2}}$ (uptake) for the case of no lens contamination, versus $-0.047\,\mathrm{kg\,C\,m^{-2}}$ when ρ_c is underestimated by 5%; this implies a 13% overestimation in the monthly uptake for the month considered.

Finally, it is worth considering the effects of errors in ρ_c on eddy covariance estimates where the WPL corrections are not applied. Some investigators convert high frequency, open-path gas density measurements to mixing ratio relative to dry air, and thus avoid the need to remove WPL terms (Bergeron et al. 2007; Giasson et al. 2006), but this does not solve the problem. Equation 17 of the original WPL paper demonstrates clearly the dependence of the calculated perturbation mixing ratio on mean ρ_c (in combination with dry air density

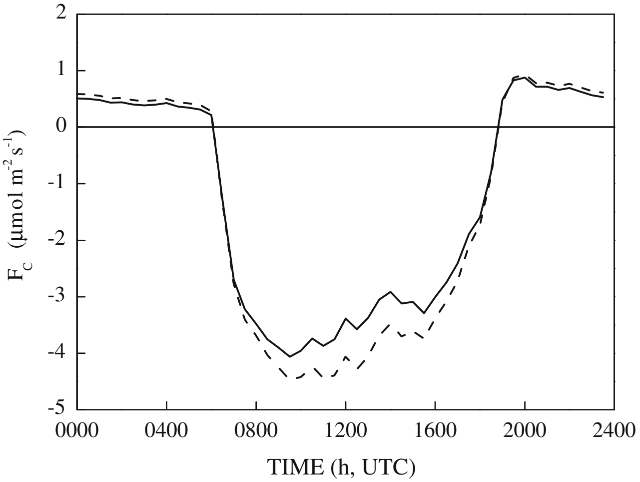

Fig. 3 Mean diurnal tendencies in the CO_2 flux (F_C, $\mu\mathrm{mol\,m^{-2}\,s^{-1}}$) for June 2004. The solid line represents the flux for clean lens conditions [presumably accurate absolute CO_2 density (ρ_c)] while the dashed line represents F_C calculated with a 5% underestimation of ρ_c due to moderately dirty lenses

fluctuations). Closed path IRGAs, on the other hand, exclude dry air density fluctuations via two steps: fluctuations associated with a temperature variation are removed during the air sampling process, while those associated with water vapour behavior are measured and excluded in the definition of the mixing ratio. Thus, closed-path IRGAs are not susceptible to errors associated with mean ρ_c.

5 Conclusions

Estimates of F_C by open-path eddy covariance are sensitive to errors introduced by the WPL terms, not only in association with the energy balance (Liu et al. 2006) but also due to inaccurate measurements of absolute ρ_c. Contamination of the optical windows of open-path IRGAs causes errors in absolute measurements of ρ_c. Such errors induce uncertainties in F_C with the same relative magnitudes as those associated with errors in the energy balance. Especially during daytime, the uncertainty in absolute ρ_c leads to sizeable underestimation of F_C by open-path eddy covariance. This diurnal bias implies a selectively systematic error that can seriously bias long-term NEE estimates towards uptake, particularly in semi-arid climates where large H_s is typical.

The underestimation of ρ_c after rain can be approximated from analogous errors in ρ_v determined versus independent measurements of absolute humidity. An empirically-determined relationship between lens contamination errors for CO_2 (the ρ_c difference before and after cleaning) and errors for water vapour (versus an independent humidity measurement) represents one means of correcting for such errors but is likely to be site-specific.

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