Supplement of Atmos. Meas. Tech., 11, 1583–1597, 2018
https://doi.org/10.5194/amt-11-1583-2018-supplement

Atmospheric Measurement Techniques
Open Access

Supplement of

Evaluation of a lower-powered analyzer and sampling system for eddy-covariance measurements of nitrous oxide fluxes

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Supplementary Materials

S1. Analyzer Calibration

S1.1 TDLAS Calibration

The TDLAS were calibrated at installation and each time the reference gas cylinder was replaced, per the procedure outlined in the user manual. That procedure is summarized below, with notes added specific to the present study.

The dominant sources of error in the TDLAS concentration measurement are the offset error caused by Fabry-Perot interference, and span errors caused by errors in reference gas analysis or by different pressure or temperature in the reference and sample cells. For eddy covariance measurements the mean concentration is subtracted; therefore the offset error cancels out and only the span errors are significant. The calibration process adjusts the span of the TDLAS.

The TDLAS span calibration requires the measurement of two calibration gases (details are given below). A five-way valve (Swagelok B-43ZF2) was used to switch between zero and span cylinders and filtered ambient air (to idle during setup). Flows and pressure regulators were adjusted to calibrate at the nominal sample cell pressure. The TDLAS parameter Reference gas concentration (ppm) was adjusted to correct the error in the measured concentration difference using:

$$C_{New} = C_{Orig}\left(\frac{T_S - T_Z}{M_S - M_Z}\right) \qquad [S1]$$

where C_{new} is the corrected reference gas concentration parameter, C_{orig} is the original reference gas concentration parameter, T_s and T_z and the true span and zero concentration, and M_s and M_z are the measured span and zero concentrations.

The initial TDLAS calibration was performed 24 June 2015 using a span cylinder containing CO_2 and N_2O in nitrogen rather than air, which can give rise to measurement error in IRGAs (Bischoff, 1974; Pearman and Garratt, 1975), and has also been shown to affect TDLAS (Bowling, et al. 2003). This cylinder was replaced with a cylinder of CO_2 and N_2O in air for the subsequent calibrations on 23 February 2016 and 18 April 2016. A cylinder of nitrogen was used as zero gas throughout the experiment.

Measurements that infer total CO_2 based on a single isotopologue can be affected by the isotope ratio, particularly when a minor isotope is measured (Tans, et al., 2017). Tans et al. (2017) derived a correction for $^{12}CO_2$ analyzers used to quantify total CO_2 when the sample has different isotopic content than the calibration gases. Adapting this approach to an analyzer that measures $^{13}CO_2$, and ignoring the relatively small effect of oxygen isotopes gives a simple approximate correction:

$$\frac{X_{Cor}}{X_{Meas}} = 1 + (\delta^{13}C_{st} - \delta^{13}C_{air})/1000 \qquad [S2]$$

Sample bags (1 L Supel inert foil gas sampling bags with screw cap valve, Sigma-Aldrich, Bellefonte, PA) were filled from the zero and span cylinders used in the field experiment and analyzed at Campbell Scientific, Logan, UT. The samples in the bags were measured simultaneously by two TGA200As, one configured for N_2O and CO_2 ($^{13}CO_2$) and the other configured for isotopic CO_2 ($^{12}CO_2$, $^{13}CO_2$, and $^{12}C^{18}O^{16}O$) measurements. During this test the TDLAS were calibrated using the two-point calibration method described in Bowling (2003). A custom valve manifold (Campbell Scientific) switched between a sample bag, a cylinder of zero air (Airgas Ultra Zero grade), and a reference cylinder of unmodified natural air obtained from the WMO/GAW Central Calibration Laboratories (CCL) located at the NOAA Global Monitoring Division (GMD). This reference cylinder (serial number CB11313) was calibrated for N_2O (WMO-N2O-X2006A mole fraction scale), CO_2 (WMO-CO2-X2007), and stable isotopes of CO_2 (VPDB scale, determined by IRMS by the Stable Isotope Laboratory, Institute of Arctic and Alpine Research, University of Colorado, Boulder (INSTAAR) (Trolier et al., 1996). Each gas was selected for 60 s, with 30 s of data omitted after valve switching for equilibration. Four cycles were recorded for each sample bag. A tee at the outlet of the manifold split the flow between the two TDLAS (100 ml min^{-1} to each). The data were processed to give a mean for each sample bag. The resulting means and ranges for the samples of span gas and nitrogen are given in Table S1.

Table S1. Mean and (range) of two sample bags for each cylinder. Values are also given for the reference cylinder used to calibrate the analyzers.

	CO_2 isotope TDLAS			X_{Cor}/X_{Meas}	N_2O/CO_2 TDLAS	
	CO_2 (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)		CO_2 (ppm)	N_2O (ppb)
Reference (CB11313)	400.38	-8.442	-3.194		--	328.81
Span in air	399.39 (0.42)	-37.00 (0.12)	-31.91 (0.02)	0.975	399.0 (0.6)	1001 (4)
Zero air (N_2)	9.98 (0.32)	-206.0 (1.8)	-27.8 (4.7)		11.8 (0.4)	8 (1)

Ambient CO_2 has a $\delta^{13}C$ of approximately -8 ‰, (Tans, et al., 2017) but it is the isotope ratio of the CO_2 flux that is of interest in the present study. Photosynthesis discriminates against the heavier isotopologue ($^{13}CO_2$) in favor of the lighter $^{12}CO_2$, and this discrimination depends on photosynthetic pathway (Farquhar, et al. 1989). O'Leary (1988) compiled results of approximately 1000 measurements of plant material $\delta^{13}C$, showing that C4 plants generally range from -11 to -15 ‰ and C3 plants generally range from -23 to -31 ‰. Dercon et al. (2006) measured isotope ratios in corn plants grown over various water regimes and nitrogen availability, with ratios from -10.8 to -12.4 ‰. Griffis et al. (2005) directly measured the isotope ratio of daytime net flux (-11.6 ‰) and nighttime respiration (-12.5 ‰) during the growing season over corn in a corn/soybean rotation. We assume an isotope ratio of -12 ‰ for the CO_2 fluxes in the present study. The correction factor X_{Cor}/X_{Meas} is given in table S1. for the span cylinder. Fluxes are multiplied by this factor in post-processing to account for this isotopic difference between the span cylinder and the fluxes.

S1.2 IRGA Calibration

This CPEC200 system was equipped with the manufacturer's optional valve module and scrub module, and the CPEC200 program parameters were set to automatically run a zero and CO_2 span sequence daily at 0:59 AM. This zero/span sequence is illustrated in Fig. S1, which shows the CO_2 and H_2O concentrations measured by the EC155.

The zero air for the IRGA calibration was supplied from a scrub module (part number 27423, Campbell Scientific, Inc., Logan UT) that includes a small diaphragm pump and a 3-stage scrubber using molecular sieve (CSI pn 27450, molecular sieve 13X, 1.6 – 2.5 mm beads, 250 g or VWR pn AAB21109-30). The scrub module removes CO_2 and H_2O from ambient air and pushes it to the EC155 at approximately 1.5 L min^{-1}. At beginning of the experiment the scrub module was refilled with a fresh molecular sieve. The scrub module received no maintenance over the entire campaign (1.5 years), although replacement of the molecular sieve is recommended annually. At the end of the experiment the scrub module was tested by setting the

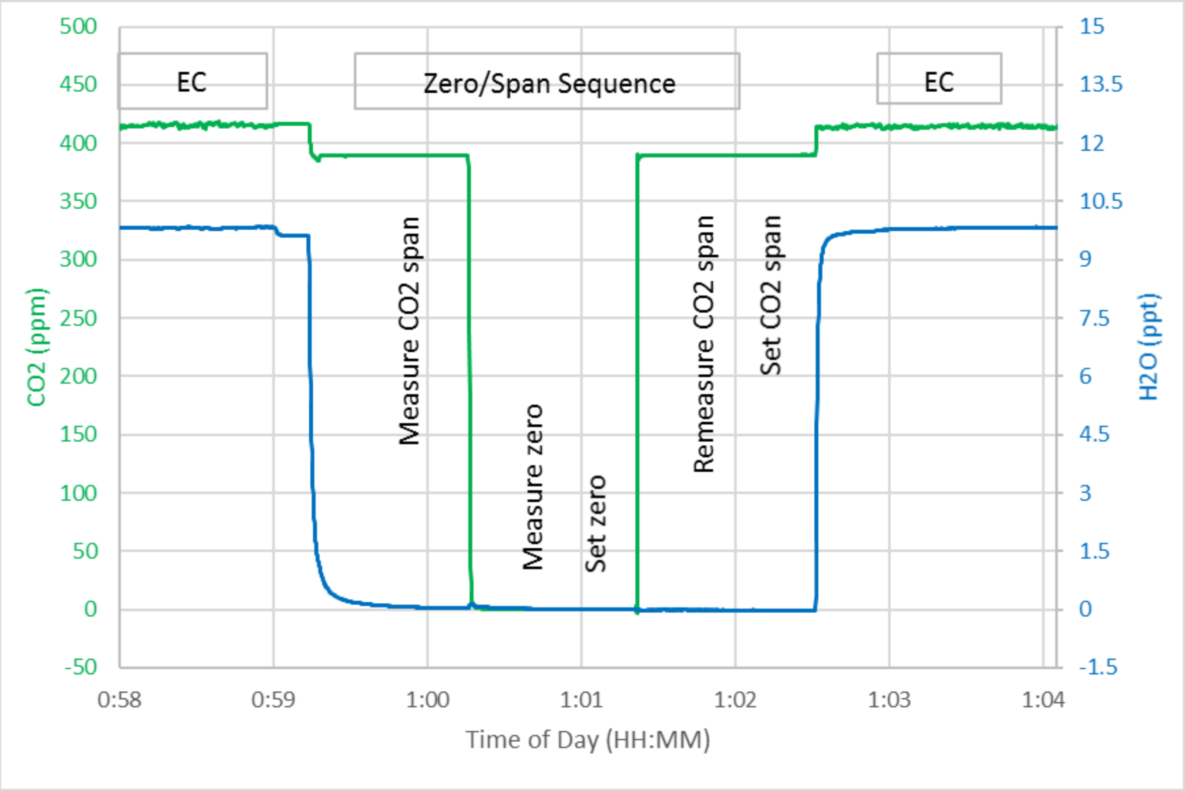

Figure S1. Example EC155 automated zero/span sequence.

zero and span of the EC155 using ultrazero grade air, reference cylinder CB11313 (Table S2), and a dewpoint generator (LI-610, LI-COR). A zero-air generator (pn 31022, Campbell Scientific, Inc.) was compared to the cylinder of zero air. The CO_2 agreed within 0.01 ppm and the H_2O agreed within 0.03 ppt, giving high confidence in the quality of the cylinder of zero air. The EC155 was then used to measure the output from each of the three stages of molecular sieve in the scrub module. The results are given in Table S2. The first stage allowed approximately half of ambient CO_2 to pass through, indicating the need to replace its molecular sieve. The second stage removed nearly all the remaining CO_2, but the final stage actually increased the CO_2, to 2.45 ppm. This was likely due to the outlet of the scrub module being uncapped for 2 months after the field campaign and before testing. After standard maintenance (replacing molecular sieve in the first bottle and rotating this to become the final stage), the scrub module removed all the CO_2. Molecular sieve has a higher capacity for removing H_2O than CO_2. Residual H_2O was very low in every case.

Table S2. CO_2 and H_2O in the air from the scrub module.

	CO_2 (ppm)	H_2O (ppt)
First stage	251.7	0.085
Second stage	0.95	0.051
Third stage	2.45	0.044
After service	-0.05	0.035

The EC155 CO_2 span cylinder was CO_2 balanced in nitrogen. The effect of an N_2-balanced cylinder as opposed to the recommended air-balance (Zhao, et al., 1997), as well as isotopic differences between the span and sample gases (Tans et al., 2017) on the calibration values was tested after completion of the field experiment.

Samples of this span cylinder were sent to CSI, Logan UT, for analysis. The EC155 was zeroed using ultrazero air and the CO_2 span was set using a cylinder of natural air (CB11313, see Table S1). The sample of the CO_2 span cylinder was measured and found to be 401.98 ppm. During the field experiment the CO_2 span parameter in the CPEC200 software was set to a preliminary value of 390 ppm. In postprocessing, fluxes measured by the EC155 were multiplied by a correction factor: 401.98/390 = 1.0307. This corrected any errors due to carrier gas or isotope ratios.

S2. Spectral Analysis

Cutoff frequencies of EC systems can be evaluated using the ratio of the spectra of a scalar of interest to that of an assumed unattenuated temperature spectra ($f_{c,s}$). This involves computing ensemble-averaged spectra or cospectra using several hours of data with conditions that warrant scalar similarity (i.e., stationary, sunny conditions with positive sensible heat fluxes, moderate winds, and a high scalar flux (Aubinet et al., 2012)). Many studies using this empirical method select data from one ideal day meeting these conditions (Detto et al., 2011; Peltola et al., 2014; Rannik et al., 2015) to calculate $f_{c,s}$ as a metric for characterizing EC systems. Unfortunately, the low N_2O fluxes observed in this study prevented an accurate analysis of the frequency response of the optimized TDLAS-TE system via spectral ratios.

One day of the study period had adequate conditions for spectral analysis (8 June 2015), i.e., consecutive 30 min periods with stationary signals, moderate winds ($2\ \mathrm{m\,s^{-1}} < U < 4\ \mathrm{m\,s^{-1}}$), strong fluxes, $|F_{N2O}| > 400\ \mathrm{ng\ m^{-2}\,s^{-1}}$), and positive sensible heat fluxes ($H > 25\ \mathrm{Wm^{-2}}$). At that time both N_2O analyzers were operating using the older-style sampling systems with nominal flows and pressures (58 and 59 mb for TDLAS-LN and TDLAS-TE, respectively). Ensemble variance spectra and cospectra of the N_2O signals were calculated using data from 13:00 to 17:00 on 8 June 2015. Cospectral analysis for the EC155 used data from a period with strong CO_2 signals ($|F_{CO2}| > 500\ \mu\mathrm{g\ m^2 s^{-1}}$, 12:00 to 16:00 on 19 Aug 2015).

Spectral cutoff frequencies were calculated by fitting the cospectral ratios of the concentration signals and sonic temperature (T_s) to a first-order transfer function (T):

$$T = \frac{1}{\sqrt{1+\left(\frac{f}{f_{c,s}}\right)^2}} \qquad \text{[S3]}$$

Results of the spectral analyses are displayed in Fig. S3. Spectra from each N_2O analyzer (Fig. S3a) were similar up to ~1 Hz where the TDLAS-TE noise became observable. Fig. S3b shows very good agreement between the N_2O cospectra as measured by each analyzer. Cospectral ratios of both analyzers were similar (Fig. S3c) and demonstrated that both analyzers captured the majority of the N_2O flux when using the older-style sampling system. CO_2 spectral analysis results for the EC155 are shown in Figs. S3 d, e, and f. Cutoff frequencies calculated by fitting equation S3 to the ratio of $Co(f)_{wN2O}$ to $Co(f)_{wT}$ gave $f_{c,s}$ = 2.5 Hz for the TDLAS-TE, $f_{c,s}$ = 2.7 Hz for the TDLAS-LN, and 3.05 Hz for the EC155. These results are not directly comparable to the in situ frequency response test because the cospectral analysis includes other losses, such as sensor separation and synchronization.

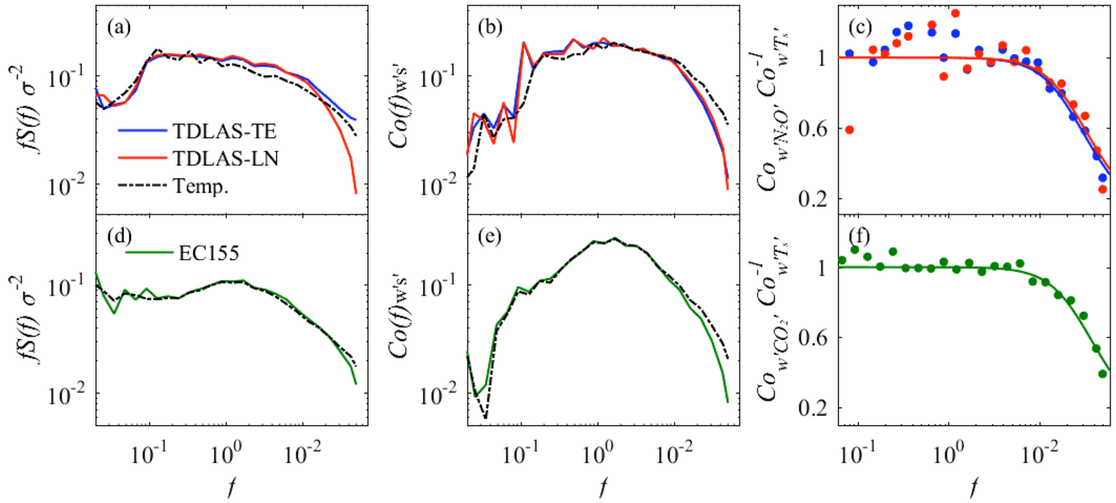

Figure S3. Results of the spectral analysis. Normalized variance spectra (Fig. S3a) and normalized cospectra (Fig. S3b), and cospectral ratios of N_2O (Fig. S3c) measured by the TDLAS-TE and TDLAS-LN for the period with strong F_{N2O} (13:00 to 17:00 local time on 8 June 2015, zL^{-1} = -0.045, u = 3.55 ms^{-1}). Figures d-f: Normalized variance spectra (Fig. S3c), normalized cospectra (Fig. S3d), and cospectral ratios of CO_2 (Fig. S3c) measured by the EC155 during a period of strong CO_2 flux (12:00 to 16:00 local time on 19 Aug 2015).

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