Supplementary material for: Correcting atmospheric CO_2 and CH_4 mole fractions obtained with Picarro analyzers for sensitivity of cavity pressure to water vapor

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S1 Uncertainties of external cavity pressure measurements in experiments with stable water vapor levels

In this section, we present possible random and systematic uncertainties of the external cavity pressure measurements, look for their signatures in data from experiments with stable water vapor levels, and quantify and discuss their impact. The purpose of this section is to investigate whether the external pressure sensor represented the pressure inside the measurement cavity with sufficient accuracy and precision to support our conclusions.

S1.1 Possible biases in external cavity pressure measurements

In this section, we discuss conceivable mechanisms that may have affected our external cavity pressure measurements.

Water-dependent bias of pressure sensor readings

Here, we give more details on possible water-dependent biases that were discussed in Sect. 4.1 of the main text for reference. Such biases may have been caused by the following mechanisms:

1. The partial pressure gradient at the drying agent may have affected external pressure sensor readings.
2. The flow through the needle valves that were used as chokes to match the pressure in the external pressure measurement line to cavity pressure may have been sensitive to water vapor.
3. The external pressure sensor may have been exposed to residual water vapor changes despite the drying cartridge.

As argued in Sect. 4.1 of the main text, the consistency of external pressure sensor readings with CH_4 as well as spectroscopic cavity pressure estimates makes it unlikely that these mechanisms affected our conclusions.

Drift of external pressure sensor readings with time

Drifts of the relationship between external pressure sensor readings and cavity pressure may have been present if the flow conditions were not stable, e.g. due to the needle valves used as chokes. This was mitigated by constantly recalibrating external pressure readings by probing dry air between each water level. Furthermore, owing to our probing strategy, a drift of

the external pressure sensor readings would have resulted in random noise. Since the residuals of the empirical cavity pressure model fits to the data were small (Sect. 3.2.1 of the main text), drifts, if present, did not affect our results.

Equilibration after changing water vapor levels

External pressure readings visibly adjusted to new levels on a timescale of minutes to roughly one hour. We attempted to characterize the timescale of equilibration, but this effort was impeded by slow drifts of the external pressure readings that could not be attributed exclusively to changing water vapor levels. Therefore, we focused on whether the largest conceivable errors could explain the pressure bend, as it was the key result of independent pressure monitoring. In particular, we repeated our analysis under the assumption that the slow drift of the external pressure sensor readings, which we had corrected for by frequently probing dry air, was an artifact of insufficient equilibration of internal and/or external cavity pressure sensor. Furthermore, we considered that changing equilibration characteristics might have created the pressure bend as an artifact of our sampling. Neither scenario can explain the pressure bend. Minor equilibration errors may explain why the uncertainties of estimated cavity pressure were smaller than the residuals of the fits to the empirical cavity pressure model (see Sect. S1.2). They correlated with residuals of CO_2 and CH_4 (see also Sect. S3), which indicates actual deviations of cavity pressure from its model rather than errors of the external pressure measurements. However, as stated above, these residuals were small and did not affect our results. We conclude that accuracy and stability of the external pressure measurements were sufficient to detect and characterize the pressure bend.

S1.2 Precision of cavity pressure estimates

We considered three different uncertainties for cavity pressure estimated based on external pressure sensor readings in experiments with stable water vapor levels: precision of the active cavity pressure stabilization system, calibration of external pressure sensor readings, and equilibration due to switching water vapor levels. To estimate their magnitude, we made use of the longest dry air measurements performed during the experiments, which lasted 5–12 hours.

Uncertainty 1: Precision of the active cavity pressure stabilization system

External pressure sensor readings varied on a timescale of seconds to minutes, which slightly influenced the 5–15 minute averages at the end of each probing interval used for analysis. The fluctuations correlated with CO_2 and CH_4 readings, and their magnitude was independent of water vapor and very similar to the standard deviations of the internal cavity pressure readings for each analyzer. This indicates that the external pressure sensor picked up variations that were due to the limited precision of the cavity pressure stabilization system. We quantified the uncertainty of estimated cavity pressure due to this limitation by varying the averaging period between 5 and 20 minutes, which yielded random variations with 1-σ-levels of 0.011, 0.005 and 0.009 hPa (68^{th} percentile of the absolute values of the variations) in the experiments with Picarro #1, #2 and #3, respectively.

Uncertainty 2: Calibration of external pressure sensor readings

To mitigate slow drift of external pressure sensor readings, we calibrated them using dry air measurements before and after a measurement in humid air. For this calibration, the readings of the external pressure sensor while measuring dry air were linearly interpolated to the averaging intervals of the measurements in humid air. We estimated the uncertainty of this interpolation by performing it on the longest dry air measurements, using random selections of the actual probing intervals. The deviations between interpolated and measured pressure were random with 1-σ-levels of 0.015, 0.012 and 0.020 hPa (68^{th} percentile of the absolute values of the variations) in the experiments with Picarro #1, #2 and #3, respectively.

Uncertainty 3: Equilibration after switching water vapor levels

After switching water vapor levels, external pressure readings needed a certain time to equilibrate. Based on our data, we could not reliably quantify this uncertainty. However, estimates for the upper limit of the impact of this uncertainty on the pressure bend indicate that it does not affect the conclusions of our study (Sect. S1.1).

Estimated lower bounds of uncertainty

Since we could only find an upper limit for the impact of uncertainty 3 on the pressure bend, we combined uncertainties 1 and 2 to provide lower limits of the error estimates for estimated cavity pressure shown in Fig. 4 of the main text. The combined error was on average 0.018, 0.013 and 0.022 hPa for measurements in humid air for the experiments with Picarro #1, #2 and #3, respectively. The residuals of the empirical cavity pressure model were larger than the estimated lower bounds of the uncertainty, by factors of 1.4 to 2.1.

S2 Uncertainties of spectroscopic cavity pressure estimates

As noted in Sect. 3.2.3 of the main text, the cavity phase length drifted over the measurement period on a scale that is comparable to the observed effect due to humidity. In Picarro analyzers, absorption lines are scanned by varying the phase length using a length actuator. This is achieved by mounting the end cavity mirror on a deformable zerodur double diaphragm, actuated by a voltage applied to a disk made from a piezoelectric material. This actuator could be susceptible to external stresses from changes in ambient pressure, local temperature, and can drift from mechanical creep. These effects should not be strongly affected by the gas sample humidity, since the actuator is isolated from the air stream by one of the zerodur diaphragms. We cannot however rule out the possibility that the humidity of the air stream affected the inner diaphragm, although we believe that this effect should be insignificant.

S3 Uncertainties of CO_2 and CH_4 measurements

Several mechanisms may have affected precision and accuracy of our trace gas measurements. Since the effect of cavity pressure sensitivity to water vapor on CO_2 and CH_4 readings is small, it was important to avoid systematic biases in our results. To randomize the impacts of various error sources, water levels were never varied monotonically throughout the experiments, so potential errors would have resulted in noise in our measurements. In the following sections, we first present possible error mechanisms and how they would – if present – have affected the trace gas readings. Then we describe observed error characteristics to infer which error sources played a role in our measurements, and whether they affected our results.

S3.1 Possible mechanisms affecting CO_2 and CH_4 measurements

Possible mechanisms that may have affected CO_2 and CH_4 readings include variations in the mole fractions delivered to the Picarro analyzer and uncertainties of its measurement system. Note that in the experiments from which trace gas data were analyzed the external pressure measurement unit was either installed downstream of the Picarro analyzer (Picarros #1 and #3), or no external pressure measurement was performed (Picarros #4 and #5), eliminating the drying agent as a potential source of error in the trace gas measurements.

Mechanism 1: Diffusion in the pressure reducer

Diffusion of CO_2 and CH_4 from high to low pressure side of the pressure reducer would likely have been visible as slow drifts over time in both dry air and humid air, or only have affected a few data points. This mechanism would likely have affected CO_2 mole fractions more than CH_4 mole fractions, because CO_2 is more prone to this effect.

Mechanism 2: CH_4 release from metal-metal friction

Metal-metal friction releases CH_4 from stainless steel surfaces (Higaki et al., 2006). This may occur when turning needle valves, tightening stainless steel tubing connections or if the stainless steel tubing wiggles after an accidental push. CH_4 released in this way to the dry line would have been washed out quickly, but could have affected the air stream through the water reservoir because of the large volume of the gas washing bottles.

Mechanism 3: Dissolution in and outgassing from the water reservoir of the humidification unit

The impact of dissolution and outgassing from the water reservoir would have depended on its characteristic timescale, ranging from reacting to short temperature fluctuations to a slow drift with time. Due to its higher solubility, short fluctuations would have affected CO_2 more than CH_4, whereas if the timescale were longer, the impact would have depended on the disequilibrium at the beginning of the experiment.

Mechanisms 4 and 5: Fluctuations of cavity pressure and temperature

Fluctuations of cavity pressure and temperature would have manifested in trace gases fluctuations with characteristic ratios of relative CO_2 and CH_4 changes, $\left(\Delta CH_4/CH_4^{dry}\right)/\left(\Delta CO_2/CO_2^{dry}\right)$. Values for this ratio were reported by Yver Kwok et al. (2015) at 2.7 for fluctuations of cavity pressure, and 1.15 for cavity temperature. In our experiment with Picarro #3, the ratio for cavity pressure changes was 3.6 ± 0.3, based on the calibration experiments presented in Sect. 3.1 of the main text.

Mechanism 6: Drifts of the optical system of the Picarro analyzer

Other drifts of the optical system of Picarro analyzers include for example small drifts in the reported mole fractions linked to the adjustment of the wavelength calibration of the wavelength monitor. Drifts can also be caused by instability of the mechanical assembly of the optics on the scale of 100 nm, as well as by variations in ambient temperature and pressure. Such drifts can be positive or negative and would affect CO_2 and CH_4 independently.

S3.2 **Observed uncertainties and impacts of individual mechanisms**

An impact of cavity pressure variations on the trace gas data (mechanism 4) could be detected in the experiment with Picarro #3, where the ratio of relative trace gas changes was $\left(\Delta CH_4/CH_4^{dry}\right)/\left(\Delta CO_2/CO_2^{dry}\right)$ = 2.6 ± 0.3. This is – due to regression attenuation – within the expected range if the true ratio is 3.6, i.e. the characteristic ratio for cavity pressure fluctuations for this analyzer. The trace gas uncertainties attributable to cavity pressure fluctuations were 0.007 ppm CO_2 and 0.1 ppb CH_4 in this experiment, based on the variability of estimated cavity pressure and its correlation with trace gas mole fractions. For the water correction experiments without independent pressure monitoring, this analysis could not be done. For these experiments, we used the uncertainty due to the precision of the active cavity pressure stabilization system following the approach for cavity pressure uncertainty 1 in Sect. S1.2. These uncertainty estimates were smaller than those of the former approach (Supplementary Table 1). Since cavity temperature fluctuations result in a smaller characteristic ratio of trace gas changes, this mechanism could not be detected.

We searched for impacts of mechanism 3 (dissolution and outgassing) by looking at room temperature variations and slow drifts over time. Room temperature was recorded only for the experiments with Picarro #5, as averages over 10 minutes. Temperatures were constant within 0.3 K in the 2015 experiment, and 2.7 K in the 2017 experiment. Water-corrected mole fractions did not significantly correlate with temperature variations, which means that dissolution or outgassing on the timescale of probing durations could not be identified as a source of systematic trace gas biases in these experiments. However, we regard this evidence with caution, since the temperature averages may not have captured short-term fluctuations of temperature experienced by the water reservoir. In particular, we speculate that the larger temperature fluctuations during the 2017 experiment may explain its larger CO_2 variability. Given that the experiments with Picarro #5 were carried out at a remote field site where temperature stability was difficult to maintain, temperature was probably more stable during the other experiments, which were performed in an air-conditioned laboratory.

We calculated trends of water-corrected mole fractions with time over the course of the experiments to investigate whether there were effects acting on longer timescales than the probing time of individual water levels. Trends we found could, owing to the sampling strategy, be treated as random noise. In one case (CH_4 in experiment with Picarro #5 from 2015), the trend explained the majority of the variability of water-corrected mole fractions. The CO_2 data from this experiment did not exhibit a trend. The pattern may be produced by a strong initial disequilibrium of CH_4 between the water reservoir and the air stream, followed by slow outgassing (mechanism 3), or by drifts of the optical systems of the Picarro analyzer (mechanism 6). Diffusion in the pressure reducer (mechanism 1) is more likely to affect CO_2, and methane release from metal-metal friction (mechanism 2) is unlikely to produce a monotonous downward trend (see below). Methane release from metal-metal friction (mechanism 2) was observed during the preparations to the 2015 experiment with Picarro #5 when adjusting the needle valves. This required long probing of the lowest H_2O level of this experiment to wash the excess CH_4 out of the head space of the gas washing bottle. It may be possible that some residual CH_4 was still present in the humid air stream for some of the data points, but unlikely to produce the linear downward trend observed during this experiment discussed above. However, since CO_2 and CH_4 results from this experiment agreed very well, it is unlikely that it caused a relevant systematic CH_4 bias.

S3.3 **Summary of the uncertainty assessment for CO_2 and CH_4 measurements**

Uncertainty attributions remained in part ambiguous, since some of the underlying mechanisms have similar effects on the data (Supplementary Table 1). In the figures, we used the uncertainties we could quantify in a meaningful way for all data points, i.e. the uncertainties due to cavity pressure fluctuations. For Picarros #4 and #5, we used the uncertainty estimated from varying the averaging intervals (same as cavity pressure uncertainty 1 in Sect. S1.2). For Picarro #3, we used the estimate based on the standard deviation of cavity pressure and its linear relationship with trace gas mole fractions in dry air instead, because it was larger. The uncertainty estimates clearly underestimate the residuals, especially for Picarros #4 and #5. However, we found no evidence for systematic biases in water-corrected mole fractions except for the aberrant CO_2 data from the experiments with Picarros #1 (droplets) and #3 (stable water vapor levels). This implies that the data were precise and accurate enough to quantify the effect of pressure fluctuations on CH_4 readings, while CO_2 remained challenging.

Supplementary Table 1: Mechanisms affecting CO_2 and CH_4 readings in our water-correction experiments and error estimates. In addition, observed uncertainties are included at the bottom of this table.

#	Description	Effect	Impact on our experiments
Potential sources of uncertainty			
1	Diffusion at pressure reducer	Trend or few affected data points; CO_2 more likely	Unlikely to have had an impact
2	Metal-metal friction	CH_4 increase in	No systematic impact found

		humidification unit	
3	Dissolution/outgassing	Trend or temperature-related fluctuations; CO_2 more likely	Picarros #1 and #3: May explain aberrant CO_2 results Picarro #5: 0.46 ppb CH_4 trend; likely either from this mechanism or mechanism 6, impact small due to sampling strategy
4	Cavity pressure variations	Characteristic ratio of CO_2 and CH_4 changes correlating with cavity pressure	Correlation of cavity pressure with dry air mole fractions (noise): Picarro #3: 0.007 ppm CO_2, 0.10 ppb CH_4 Varying averaging intervals (noise): Picarro #3: 0.004 ppm CO_2, 0.05 ppb CH_4 Picarro #4: 0.006 ppm CO_2, 0.06 ppb CH_4 Picarro #5: 0.003 ppm CO_2, 0.05 ppb CH_4
5	Cavity temperature variations	Characteristic ratio of CO_2 and CH_4 changes correlating with cavity temperature	No impact found
6	Drifts of optical system		See mechanism 3
Observed uncertainties			
	Standard deviation of dry air measurements		Picarro #3: 0.011 ppm CO_2, 0.16 ppb CH_4
	Uncertainty of corrected wet air mole fractions (lowest values of all models)		Picarro #3: 0.014 ppm CO_2, 0.16 ppb CH_4 Picarro #4: 0.016 ppm CO_2, 0.21 ppb CH_4 Picarro #5: 0.010 ppm CO_2, 0.17 ppb CH_4

References

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