

Authors response to referee comments

O'Shea, S. J., Bauguitte, S. J.-B., Gallagher, M. W., Lowry, D., and Percival, C. J.:
Development of a cavity enhanced absorption spectrometer for airborne
measurements of CH₄ and CO₂, Atmos. Meas. Tech. Discuss., 6, 1-41,
doi:10.5194/amtd-6-1-2013, 2013.

We are grateful to both anonymous referees for their helpful comments about the manuscript. We now address the comments individually. For clarity referees comments are coloured red and the responses are coloured black.

Referee #1

Note that the gas pressure in the measurement cell for LGR's commercial Greenhouse Gas Analyzer (CH₄, CO₂, H₂O) is generally controlled at 142 torr. However, to allow for measurements on-board aircraft flying up to 9150 meters, as investigated in this paper, the set-point gas pressure in the cell was reduced to 50 torr to allow for measurements over the entire flight trajectory. As a result, for this particular instrument, the change in gas pressure in the measurement cell decreased the measurement precision by about a factor of two compared with the standard commercial instrument.

The reviewer is correct that one of the reasons we choose to control the instruments cavity pressure at 50 Torr is it allowed the instrument to be successfully operated over the full altitude range of the aircraft. However, we did not determine such a large difference in precision between operating the instrument at 50 Torr and 142 Torr, certainly not as large as the factor 2 suggested by the reviewer. This is explicitly mentioned in the revised manuscript. To assess this we compute Allan variances on the systems measurements sampling air from a tank in the laboratory, 1 Hz (1 σ) precisions of 1.88 ppb for CH₄ and 0.41 ppm for CO₂, were typically obtained at 50 Torr operation. This compared to 1.59 ppb for CH₄ and 0.31 ppm for CO₂ at 142 Torr operation. Please note that LGR updated pressure broadening coefficients according to each cavity pressure setting, to ensure accurate spectral fits from their online data analysis software.

Unlike the older instrument described in the present paper, commercial instruments now available from LGR include, as standard, data analysis software that provides accurate reporting of methane and carbon dioxide on dry (and wet) mol basis continuously and directly (without post processing). These gas concentrations are obtained from the fully resolved absorption (methane, carbon dioxide and water vapor) lineshapes measured by the instrument and accurate water vapor pressure broadening information.

Our FGGA system was procured in July 2009 and came with its online processing of dry mole fractions as described in Section 2.4. We explained that the LGR software water dilution algorithm alone (Eq 2) is insufficient for reporting accurate dry mole fractions (Fig. 5). We acknowledge that newer versions of the LGR online data processing software may include a more robust water correction algorithm as suggested by the referee. To our knowledge, LGR have not published their detailed methodology for dry air mole fraction reporting in their latest GHG analysers (e.g. enhanced-performance GGA), or/and an assessment of how well this new revised algorithm is performing. It is important to build statistics on the stability and transferability of these algorithms across multiple instruments. This is starting to be done for instruments from Picarro. Inc employing the cavity ring down spectroscopy technique (CRDS, see Rella et al., 2013), however this has not yet be done for instruments employing the CEAS techniques.

Finally, a more reliable and accurate method of generating known gas concentrations at different humidity values involves using a Nafion dryer (in reverse) and a Dewpoint Generator. In this scheme, dry gas of known concentration is directed through the center bore of the Nafion tube while wet "zero" air at different humidity values from a Dewpoint Generator is directed through the outer sheath of the Nafion. This method allows the control of both the dry gas concentration as well as the water vapor concentration and, most importantly, avoids solubility effects (particularly for CO₂) that can occur when flowing dry gas through the Dewpoint Generator, that can occur using the method described in the paper.

We thank the reviewer for their suggestion on how to produce for a particular species a gas mixture with a variable wet air mole fraction and constant dry air mole fraction. We will incorporate his/her described method into our on going tests to determine the stability of the correction functions. However, we do not expect the solubility of CO₂ in H₂O to have a large effect, since we placed a dryer (dry ice trap) downstream of the Dewpoint generator allowing the dry air mole fraction of humidified gas mixture to be monitored at regular intervals. Also, the humidifier used in this work has previously been used in several previous studies where similar tests were performed, CO₂ solubility was not found to be a large problem (Chen et al., 2010).

Referee #2

This paper by O'Shea et al. focuses on the development of airborne measurements of CO₂ and CH₄ using the cavity enhanced absorption spectroscopy technique, and have improved/discussed several important aspects that are essential for making high accuracy airborne measurements of CO₂ and CH₄: 1) design of the inlet system and characterization of the flow system; 2) application of gas standards and calibration system; 3) development of correction functions to convert wet mole fractions of CO₂ and CH₄ to dry mole fractions; 4) validation from comparison between in situ and whole air sample measurements. Although similar work for several other techniques has been done and published, it is particularly useful for researchers who are interested in implementing

the cavity enhanced absorption spectroscopy technique. This paper is well written and needed, and I can recommend publication after addressing my comments below.

General comments

1) The characterization of the uncertainty of 1Hz measurements should include not only the uncertainty of the measurements of calibration/target gases, but also the uncertainty in the water corrections in the case of wet air measurements. Besides this, it should also include the uncertainty of the calibration scale.

We have now included these additional uncertainties in the calculation of the total uncertainty.

2) the introduction gives sufficient background for why airborne CO₂ and CH₄ measurements need to be made. However, no information about available techniques is mentioned. As this is a technical paper, it will read better if some basic discussions of available techniques are briefly discussed.

We agree and have added a paragraph on this subject to the introduction.

3) the units for CO₂ and CH₄ should be ppm and ppb, not ppmv and ppbv because the WMO scales for CO₂ and CH₄ are defined in ppm and ppb, not ppmv and ppbv.

This has been changed in the revised manuscript.

Specific comments

P2/L8-11: please refer to the general comment #1

These numbers have been changed so that they now include additional uncertainties described in general comment 1.

P7/L7-9: how was the flow controlled at constant volumetric flow rate of 0.8 Lpm? Was it not mass flow rate?

The referee is absolutely correct: we have verified in the laboratory that constant sample mass flowrate is maintained. Although no mass flow controller was used as illustrated in the systems plumbing in Figure 1, the combination of the Pneutronics VSO electronic pressure controller and KNF diaphragm stabilization system of the external pump (high suction speed) clearly contribute to the observed performance.

P7/L9: at 9150 m, the ambient pressure is still much higher than the cavity pressure setting of 50 torr, I wonder why the cavity pressure cannot be controlled without opening the throttle valve?

At 9150 m, the pressure differential across the orifice of the electronic pressure controller

(~220 mb) has reached its critical flowrate. The sample flow can no longer be maintained, causing the FGGA cavity pressure to drop. This is effectively a hardware limitation. The cavity pressure control could indeed be recovered by opening the throttle valve as suggested by the referee, and this was tested successfully in flight. However, this requires operator manual control of the throttle valve, which is less than ideal in the tight environment of our rack-mounted instrumentation. Opening the manual throttle valve also has the disadvantage of increasing the sample flowrate, requiring further adjustments for instance to the calibrant overflow during in-flight calibrations above 9150 m. We instead accepted the 9150 m altitude operational ceiling for fully calibrated measurements, but will in the future attempt to push this altitude limit to that of our research aircraft (10670 m).

P9/L5-8: Again about the flow rate, if it was maintained at a constant mass flow rate, the theoretical inlet lag time (assuming plug flow) at 287 mb should be 3.5 times smaller than that at 1007 mb, and experimental results showed only two times smaller, but with a relatively large uncertainty. Will it be better to just use the theoretical inlet lag time? It does not make sense if it was maintained at a constant volumetric flow rate.

The referee is correct in pointing out that there should be a factor 3.5 difference in inlet lag time when sampling at 1007 mb and 287 mb. Using the now ascertained constant sample mass flow rates we calculate theoretical (plug-flow) lag times to be approximately ~ 4.6 s at 1007 mb and ~ 1.3 s at 287 mb, which is within the uncertainties of the experimental results. The theoretical lag times are now mentioned in the revised manuscript. We have found that for most applications a 1s inlet lag time uncertainty is acceptable.

P11/L15: please double check the use of the term “certification”. “calibration” should be sufficient.

This has been changed.

P12/L6-8: has any correction been applied to the measurements to account for the drift of the cylinder? And how?

No long-term drift correction (arising mostly from high/low CO₂ calibrations) was applied to our data. This was justified by the good agreement of all in flight targets, with a mean of -0.06 ppm. It is worth noting that we have good confidence in the calibrated target gas concentration, with no observable drift between IMECC and Royal Holloway calibrations as depicted in Table 1.

P15/L19-21: It is interesting to see there is such a high linear correlation between the water vapor measurements from the dew point generator and the FGGA analyzer. Can the author give any explanation about why the intercept is -0.65%, not close to 0%? What will be the water vapor reading if gas from a cylinder is provided to the FGGA analyzer? I understand the dew point generator is not highly accurate, but the uncertainty on the

temperature measurements by the dew point generator should be relatively small, not enough to explain such a big intercept.

Neither the dew point generator nor the FGGA's H₂O measurements were calibrated directly before these experiments. The high linear correlation would suggest that both instruments have approximately linear responses to changes in H₂O. When sampling the gas stream that had passed through the dry ice trap the FGGA records a mean H₂O content of 0.013 % ($1\sigma = 0.008$ %), possibly attributing much of the off-set to the dewpoint generator. This is now mentioned in the revised manuscript. However, as noted in the manuscript highly accurate H₂O measurements are not needed for the correction functions to work successfully.

P16/L14-17: when comparing to similar test results on the CRDS analyzers shown in Chen et al., 2010, Winderlich et al., 2010, Nara et al., 2012, the residuals here are relatively large. Do the authors understand what caused the relatively large residuals?

CH₄ residuals in this experiment are generally comparable to studies using CRDS and CO₂ residuals are slightly larger (Rella et al., 2013). We aren't able to explain specific reasons for the differences in the size of the residuals between this study and those using CRDS. Experiments are ongoing to improve statistics on the size of the residuals.

P16/L17-19: this sentence has been said in L10-12

This sentence has been removed from L10-12.

P18/L3: remove "precision" as this does not need to be estimated from examining the difference.

This has been removed.

P18/L17: remove "The FGGA system was remarkably robust" / give objective numbers to show the robustness.

A contrast between laboratory and in-flight operation has been made in the revised manuscript.

P18: after reading the section 3.1, I have no idea what is the standard deviation of the FGGA measurements for CO₂ and CH₄ under lab conditions and during flight calibration measurements. Can the authors provide such information?

See response to previous comment.

P21/L19-22: please refer to the general comment #1

These numbers have been changed so that they now include the additional uncertainties described in general comment 1.

P31/Table 1: “A 6 month mixture stability check showed the standards were stable over this period” is not accurate. Please indicate the relatively large drift of 0.17 ppm for the Low gas.

This has been reworded.

P38/Fig. 5: clarify that the data shown in this figure are averaged values, not 1 Hz response : : :

This is correct and has been changed in the revised manuscript

P39/Fig.6: precision is not estimated from the differences, and please refer to the general comment #1 for the accuracy discussion

This has been changed in the revised manuscript.

Technical corrections

1) P2/L2, P5/L15, P21/L16: “onboard” ! “on board” or “aboard”

These have been changed.

References

Chen, H., Winderlich, J., Gerbig, C., Hofer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO₂ and CH₄) using the cavity ring-down spectroscopy (CRDS) technique, *Atmospheric Measurement Techniques*, 3, 375-386, 2010.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.*, 6, 837-860, doi:10.5194/amt-6-837-2013, 2013.