

## **Author Response to Anonymous Referee #2**

**We thank the reviewers for their useful and constructive comments. We shall address each of the reviewer's comments in turn. Reviewers comments are coloured red and the responses are coloured black.**

**All page/line numbers refer to the position in the amended manuscript, available on the interactive discussion page.**

### **General Comments:**

In this paper, Pitt et al. describe the use and characterisation of a Quantum Cascade Laser Absorption spectrometer (QCLAS) on the UK FAAM large research aircraft for in situ measurements of methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ). The atmospheric importance of these two species is well known and is covered appropriately in the Introduction. Continuous analysers already exist for measuring atmospheric methane mole fractions and have been deployed on this aircraft (such as the cited Fast Greenhouse Gas Analyser (FGGA), which also measures carbon dioxide). The successful deployment of an instrument for measuring atmospheric concentrations and fluxes of  $\text{N}_2\text{O}$  is especially welcome. Its installation on an aircraft allows the estimation of  $\text{N}_2\text{O}$  fluxes from important disperse or area sources, such as wetlands (for  $\text{CH}_4$ ) or agriculture (both  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ).

Two main instrumental issues were investigated: (1) the need to correct for the effect of water vapour on the spectral absorption lines, and (2) the origin and correction of pressure effects. The availability of the Fast Greenhouse Gas Analyser (which has been previously calibrated to WMO standards) and the use of reference gas mixtures of known concentrations has allowed the precision and accuracy of the QCLAS to be established.

Overall, the paper is well written and should be published after addressing the specific and technical comments below.

### **Specific Comments:**

In the Introduction (p. 8862), many of the cited papers on airborne measurements refer to methane. It would be useful to know which greenhouse gases were measured in the different studies. This would also help to emphasise the lack of measurements on  $\text{N}_2\text{O}$  (and hence the selection of  $\text{N}_2\text{O}$  for the case study).

This is a useful comment. We agree with the reviewer that it is important to highlight the need for increased deployment of instruments measuring  $\text{N}_2\text{O}$  on board aircraft. We have added a sentence to emphasise this (P3/L31 – P4/L2), which notes that only two of the studies mentioned made continuous in situ  $\text{N}_2\text{O}$  measurements. However, we feel that listing all the measurements made in each study would have a detrimental effect on the readability of the section as many of the studies listed made measurements of a wide variety of greenhouse gases and related compounds (too many to effectively and consistently list).

### **Water–Vapour correction**

As is standard, a water–vapour correction (Section 2.4) is applied to report the measurements as dry–air mole fractions and thereby remove any effects arising from large changes in ambient water vapour concentrations. The first approach used built on work by the same group using the FGGA, as reported in the cited paper by O’Shea et al. (2013b). In that paper, the use of a nafion drier is also described and the decision taken to remove it. In the current paper, there are clearly issues with long–term stability, with the July 2014 calibration results differing significantly from the initial set made in November 2013. I did not altogether find the the discussion on this completely clear. Are the authors suggesting that the spectral intensity of the laser is changing? There are no spectra presented to show that the absorption lines are distinct and therefore give a good measure of the baseline. It is simply stated that a region between 1275.3 and 1275.8 cm<sup>–1</sup> contains ro-vibrational transitions of N<sub>2</sub>O, CH<sub>4</sub> and H<sub>2</sub>O (p. 8865).

We apologise for the lack of clarity here and we have amended the discussion to improve this (P11/L10 – L20). To clarify, we believe that the issues with long-term stability are associated with a lack of stability in the uncalibrated measurement of H<sub>2</sub>O mole fraction. This is evidenced by the drift in the measured H<sub>2</sub>O mole fraction during our “dry” laboratory runs seen in Fig. 2. As this is a measurement of very dry air (less than – 60°C), this drift can be assumed to represent a measurement of the variability in baseline structure in the region of the H<sub>2</sub>O absorption line. It is difficult to de-convolve the different factors that could be responsible for this baseline structure variability; it could be associated with changes in laser or detector response, but a further possibility is that fringes caused by reflection of the beam from plane parallel surfaces in the optical path (i.e. an etalon effect) move across the spectrum under changing environmental conditions, as a result of slight changes in the optical alignment and pathlength (see also our response to Referee 1).

Our discussion concerning this baseline drift in the region of the H<sub>2</sub>O peak has been expanded in the amended manuscript (P11/L10 – L20) , along with a discussion explaining why this contributes to the superior performance of the spectroscopic water vapour correction over the scale factor method (P12/L3 – L21).

A second method is investigated based on the vendor TDLWintel software. This makes a significant improvement to the retrieved mole fractions. Why was this not used initially? What are the advantages and disadvantages of the two approaches? More discussion is needed here. If I understand correctly, the water broadening coefficients of 1.6 and 1.8 for CH<sub>4</sub> and N<sub>2</sub>O, respectively, are not absolute values (in which case, the units are missing) but relative to the air-broadening coefficients. Is this correct?

A spectroscopic water vapour correction was added in a recent update to TDLWintel, and was not available when we first operated the instrument on the FAAM aircraft. The scale factor method was adopted initially based on good results achieved using this approach on similar instrumentation (e.g. by Rella et al., 2013; O’Shea et al., 2013b; Zellweger et al., 2012). Therefore, we feel that a comparison of the two methods was instructive to other experimentalists that may seek to apply similar corrections, informing best practice based on

our comparison. A section discussing why the spectroscopic correction produces superior results has now been added to the amended manuscript (P12/L3 – L21).

Regarding the comment on line broadening, the reviewer is correct that the water broadening coefficients are relative to the air broadening coefficients. The manuscript has been amended to clarify this (P10/L5 – L8).

### Pressure effect

A pressure effect is observed leading to large changes in retrieved atmospheric mole fractions over short periods of time. This is linked to changes in cabin–air pressure and further tests suggest that the changes in cabin–air pressure affect the optical alignment of the spectrometer. This was found to be a major term in the error budget. An approach is developed which effectively removed this effect, albeit at the expense of data capture. Calibration measurements made at the relevant pressure levels are used and as the authors acknowledge can be several hours apart from the actual measurements. Clearly, more frequent calibration would help to address this issue. Are there reasons why this was not done? Further work (outwith this paper) is needed on this topic as the authors acknowledge that potentially useful data are removed when rapid pressure changes occur, e.g., during vertical profiling or aircraft manoeuvres.

Unfortunately the cause of the large drifts observed in the data was not diagnosed until after the end of the 2014 flying campaigns, partly due to the lack of cabin pressure data available, and as such we were not able to adapt our calibration strategy accordingly during this period. In the 2015 flying campaigns, armed with the new cabin pressure data and a hypothesis as to the cause of the observed drift, we were able to perform span calibrations at each new cabin pressure, thus significantly increasing the data coverage of quality-assured (traceable) data. Data during profiles is still flagged as poor quality, and developing a consistent calibration regime that improves data coverage further is a priority for future work. Further test flights are planned for early 2016 to evaluate the suitability of using frequent spectral background measurements (i.e. zero air) to account for the observed changes in baseline structure.

The authors should clarify 'these campaigns' (p. 8874, line 22). Presumably, the pressure was not recorded during the 2014 campaigns.

The reviewer is correct – this has now been changed to clarify this (P15/L3).

### Case Study

An illustrative case study is included (Section 4). As discussed in the paper by the same group (cited paper by O'Shea et al., Atmos. Phys. Chem., 2014), the FGGA methane measurements were used to estimate a regional–scale methane flux from Scandinavian wetlands. I would very much have liked the case study presented here to have been expanded to give some idea of the fluxes. This would have required discussion of the methods (possibly involving atmospheric chemical transport models). At a minimum, it would be useful to know (with assumptions made on wind speed and boundary-layer height), the minimum detectable fluxes of nitrous oxide (and methane) implied by the QCLAS precision and

accuracy and how these compare with emission estimates from the UK national inventory for this region.

We agree that a case study of calculated fluxes would be a useful piece of science. However, the calculation of a flux for N<sub>2</sub>O (and CH<sub>4</sub>) is not at all trivial (see our papers, e.g. O'Shea et al., 2014a) and would represent many additional pages and a self-contained study, which would be beyond the scope of this technical paper (and the scope of AMT), as stated in P18/L19 – L22, and would confuse the technical advice we offer here. We anticipate that further papers will follow that will discuss such fluxes using our measurements but for now we would like to release this paper as a technical study to aid other users and not to confuse technical advice with case study output (which would be better suited to a journal such as ACP). We feel that the presentation of a limited set of field data (as we have here) is useful and sufficient to highlight the type of measurements we can do and allows us to allude to what science can be done with the measurements in follow-on studies that make use of our existing and future measured datasets from the FAAM aircraft.

#### **Technical comments:**

There is a tendency to use the name of the instrument manufacturer as an adjective describing the instrument (e.g., "Aerodyne Research Inc. Quantum Cascade Laser Absorption spectrometer" or "Los Gatos Fast Greenhouse Gas Analyser"). This is very clunky. It is more normal practice to describe the instrument and put the manufacturer and model in brackets. This is done elsewhere in the paper, for example, thermoelectrically cooled photovoltaic detector (Vigo Systems, Poland).

This has been changed as suggested in the amended manuscript.

There are minor typographical errors and other comments:

- p. 8862, line 17: "top-down" measurement could insert atmospheric to re-inforce the point that atmospheric measurements can be used to constrain surface emission fluxes.

Agreed. Changed as suggested.

- p. 8863, line 17: "small" in "small instrument response time" should be replaced with "fast" or similar.

Agreed. Changed as suggested.

- p. 8863, line 18: "optics and detectors available at near-IR wavenumbers of 6000 cm<sup>-1</sup> " should be rephrased to, e.g., "optics and detectors available in the near-IR region around 6000 cm<sup>-1</sup> ". One could also give the wavelength.

Agreed. Rephrased as suggested.

- p. 8874, line 26: "was flown to further understanding of the underlying issues" needs to be rephrased.

Rephrased to “In April 2015 we performed a test flight (B903) designed to further understanding of the underlying issues behind the large gradients in QCLAS CH<sub>4</sub> data described in Sect. 3.1 above.”

- Figures 7 and 8: Add flight number to figure captions

Flight numbers added.

## References

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 CH<sub>4</sub> and CO<sub>2</sub>, *Atmos. Meas. Tech.*, 6, 1095–1109, doi:10.5194/amt-6-1095-2013, 2013b.

O’Shea, S. J., Allen, G., Fleming, Z. L., Bauguitte, S. J.-B., Percival, C. J., Gallagher, M. W., Lee, J., Helfter, C. and Nemitz, E.: Area fluxes of carbon dioxide, methane, and carbon monoxide derived from airborne measurements around Greater London: A case study during summer 2012, *J. Geophys. Res.-Atmos.*, 119, 4940–4952, doi:10.1002/2013JD021269, 2014a.

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.

Zellweger, C., Steinbacher, M. and Buchmann, B.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, *Atmos. Meas. Tech.*, 5, 2555–2567, doi:10.5194/amt-5-2555-2012, 2012.