

## Response to Referees

### **“A Fourier transform infrared trace gas analyser for atmospheric applications” by D. W. T. Griffith et al.**

We thank both referees for constructive comments which will improve and clarify parts of the paper. We provide here explicit responses to all reviewer comments, and attach a draft revised manuscript incorporating these responses. Changes are highlighted in red throughout the manuscript.

#### **Reviewer 1 and 2 General comments**

It is true that brief descriptions of the FTIR analyser have been published previously but only in outline in earlier papers focussed on applications. Here we provide for the first time a comprehensive description of the analyser, which we think appropriate to the GGMT special issue of AMTD. Isotopic calibration, as presented at the GGMT meeting, is included in detail (an early version was contained in an appendix to Griffith et al. “The UoW FTIR trace gas analyser: comparison with LoFlo, AGAGE and tank measurements at Cape Grim and GASLAB”, in: Baseline Atmospheric Program (Australia) 2007-2008, edited by: Derek, N., and Krummel, P., Australian Bureau of Meteorology and CSIRO Marine and Atmospheric Research, Melbourne, Australia, 7-22, 2011.) Performance characteristics are described comprehensively, with a review of selected applications kept brief to achieve an acceptable length of the paper. This paper is complemented by that of Hammer et al. describing the particular application to background air measurements in the ICOS programme (“Assessment of a multi-species in-situ FTIR for precise atmospheric greenhouse gas observations”, Atmos. Meas. Tech. Discuss., 5, 3645-3692, 10.5194/amtd-5-3645-2012, 2012).

#### **Reviewer 2**

*The number of figures (17) is quite high, and sometimes their very short descriptions (in text and captions) are inadequate for the non-expert reader. If the abbreviated descriptions are due to a page limit, my suggestion is to eliminate some of the figures and provide additional explanation of those that remain. For example, there are four figures showing chamber experiment results but only 27 lines of text that explain them. Figures 16 and 17 are described with only 8 lines of text.*

To keep to an acceptable length, we have expanded captions to figures rather than main text. We have removed Figure 8. Fig 11 and its accompanying text could be removed if the editor feels the paper is too long – see comment on this section below (P3737). The text for the second chamber example has been substantially rewritten and we have removed Figure 16.

*The paper touts the FTIR analyzer as capable of “continuous” measurements, but presents measurements and results based on spectra co-added for periods of 1 minute or more to achieve adequate signal to noise. That is indeed a good data rate, but also similar to fast gas chromatography measurements described in this paper as “pseudo continuous”. In my opinion the term “continuous” overstates the capabilities of the analyzer throughout this paper and should either be tempered or removed.*

A GC takes a snapshot of the atmosphere for each injection and analysis – GC measurements made regularly over a time period are pseudo-continuous. The GC measurement series contains no information about the atmosphere between injections, it is discontinuous. Optical instruments such as the FTIR and laser analysers make continuous measurements of a stream of sampled air and determine the mean concentration over an averaging period. The measurement contains information throughout the averaging period and in this sense is “continuous”; there is always a minimum measurement time and an averaging period at some timescale. Laser techniques, such as ICOS and CRDS, average many hundreds or thousands of individual measurements (scans or ringdowns respectively) to provide each reported measurement datum, even at their highest time resolution. FTIR is somewhat slower, it averages 1-s measurements, but the principle is the same. What may be considered effectively “continuous” depends on the measurement problem – if the system being studied varies on a timescale of 10 minutes, 1 min average measurements are effectively continuous. If the natural variability is on a 10 s timescale, 1 min does not capture the high frequency variability is not effectively continuous. For baseline clean air measurements 10 minute averaging is generally fine.

To respond to this comment (and others made below on the same point) we have changed the text to stress that a measurement is a time average whenever the sense is individual measurements, keeping “continuous” for the sense of uninterrupted automated measurements over a time period.

*At several points in the manuscript I questioned why the air stream into the analyser was necessarily dried, with the exception of measuring water vapor (and its isotopes). Do the absorption lines of water vapor greatly interfere with those of the targeted trace gases? Are water vapor lines saturated, making it difficult to calculate the dry mole fraction of trace gases without independent water vapor measurements? This important conceptual point is overlooked in the manuscript, and I feel there is a need to include some information about it.*

Water vapour features are never entirely absent from the spectra, even at levels of a few ppm, and are always co-fitted in the spectrum analysis. All trace gas mole fractions can be retrieved from spectra of undried air, but with increased uncertainty due to uncertainty in the water vapour corrections described in section 3. This is sufficient to reduce accuracy to an extent important for GAW-compatibility targets, so for these measurements drying is recommended. We have added words to section 2 (drying, spectrum analysis) and 3 (cross sensitivities) to clarify this point.

*“Determine the fractionation” appears several times in the manuscript to describe measurements of the stable isotopic composition of a trace gas. Although this terminology is technically correct, the reader may be confused into thinking that you are measuring the influences of a process on isotopic composition rather than the isotopic composition itself. One of the benefits of the FTIR analyzer is that it can measure the absolute abundances (i.e., mixing ratios) of the isotopologues instead of just their ratios. This should be clearly emphasized in the manuscript. This is a minor point, but I greatly prefer “determine the isotopic composition” instead of “determine the fractionation”.*

We have changed “fractionation” to “composition” or “amount”, as appropriate, throughout the MS.

*In the abstract the analyzer is described as capable of making “high precision and accuracy” measurements. The precision of measurements is fairly easily established, but the accuracy is not. Nowhere within this paper is an attempt made to estimate the accuracy of measurements. Comparisons with established calibration standards (reference gases) are mentioned, qualitatively e.g., “good agreement”), but nothing quantitative is presented. How can you tout the analyzer’s ability to make measurements with “high accuracy” without providing quantitative evidence?*

In the section “Calibration and accuracy” in section 3 we describe the absolute accuracy in terms of firstly the “raw” FTIR scale (accurate to only a few percent), and accuracy as obtained by measurements of standard reference gases. (In the original submitted MS, we stressed *precision* and *accuracy* in this paragraph by use of italics to make the distinction clear. Unfortunately the italics were removed in the published paper.) While it is true that reference gas measurements are not described in detail in this paper, we refer to Hammer et al 2012 where this is treated exhaustively, and reproduce in Figure 5 a relevant Figure from that paper.

We have amended the reference to accuracy in the abstract and added an explicit sentence to the section Calibration and Accuracy to refer to the comprehensive assessment of accuracy in the accompanying paper by Hammer et al.

*Specific comments:*

*Page 3718 Lines 15-16 (P3718 L15-16): The connection between “isotopic tracer experiments” and “for example  $^{13}\text{C}$  in  $\text{CO}_2$  and  $^{15}\text{N}$  in  $\text{N}_2\text{O}$ ” is not at all clear. What is the relationship between these stable isotopes and “isotopic tracer experiments”?*

We have clarified this sentence.

*P3719 L9-11: This makes it sound like  $\text{CH}_4$  and  $\text{N}_2\text{O}$  don’t accumulate in the atmosphere.*

Good point, we have clarified this sentence.

*P3720 L15-16: Optical techniques like ICOS or CRDS are well suited to continuous measurements, but FTIR spectroscopy requires a fair bit of signal averaging to obtain adequate measurement precision.*

Please see earlier comment.

*P3720 L19-20: If a laser is a “single wavelength device” how can it be scanned over a “narrow wavelength interval” ?*

A laser emits a single wavelength at any one time – this wavelength may be scanned over a narrow range by changing typically temperature or current through the laser. The laser wavelength is scanned over the target absorption line to make a single measurement of concentration. See comment above (P3720 L15-16).

*P3721 L16: Is “clean” air the same as “background” air or has it been scrubbed of some gases?*

It is whole air from a clean, but not necessarily baseline site. We have added “whole” to the description.

*P3725 L3-4: If the water vapor mixing ratio in dried air is <10 ppmv then the correction to the dry mole fraction is <0.001% (not just “small”).*

Correct, but the correction is made for completeness, and may become relevant as water vapour increases above the optimum (eg when the perchlorate becomes exhausted). We have changed “small” to “negligible”.

*P3726 L8: All versions of the Beer-Lambert Law that I can find state that the absorbance is directly proportional to the absorber concentration, not “approximately proportional”. There may be deviations from linearity under certain conditions, but Beer’s law has an equal sign.*

This is correct, we removed “approximately”.

*P3729 L6-13: The “wide range of mole fractions” in Figure 5 isn’t very wide for CO<sub>2</sub> or N<sub>2</sub>O (only 10-20%). This section (3.2), although entitled “Calibration and accuracy”, doesn’t quantitatively address accuracy, either in terms of agreement with the U of Heidelberg reference tanks, or in terms of absolute accuracy (i.e., what are the uncertainties of the reference tanks and how do they propagate to the absolute accuracy of the FTIR measurements?).*

Griffith et al., 2011, referred to in the text, cover a much wider range of mole fractions for each species than Hammer et al. We have removed the word “wide”. Please see earlier response to comment on accuracy.

*P3734 L25: I see 4 reference tanks in Figure 7b (not “5”) and this is confirmed in the Figure caption.*

On checking, we found data for the two figures stemmed from calibrations run under different conditions – for this we apologise. We reanalysed the data collected for figures 7 (a) and (b) for consistency between the empirical cross sensitivity determination (7a) and the calibration (7b) and have remade the figures. We have also partly reworded the last paragraph of this section for greater clarity.

*P3735 L5-17: This is an awkward place for the section 3.5 “Cross sensitivities” (immediately after a long discussion of  $^{13}\text{C}$  measurements). Would this section fit better before the isotope discussion?*

Good idea, we have moved the cross-sensitivity section ahead of the isotopic calibration section and made minor changes to fit better to the new location.

*P3736 L2: Again, “continuous” is overstating the capabilities of the FTIR analyzer, especially in this background monitoring application.*

Please see earlier comments on the meaning of “continuous” measurements.

*P3736 L10: Identify here that “AGAGE measurements” are “GC” and in Lines 13-14 mention for which type of “GC detector(s)” you are discussing response non-linearity.*

CO by AGAGE-GC is measured with the  $\text{HgO}$  reduction detector – well known to be non-linear. Since submitting the original manuscript the AGAGE data have been recalibrated and the calibration offset is no longer evident (Paul Krummel, CSIRO, pers. comm.). We now present the data with updated calibration. Since the original Fig 8 overview has been dropped, we present the comparison data over the whole 3 month period rather than the short 2-week example previously shown.

*P3736 L20: Presumably the locomotive is electric, not diesel, and there are no influences of train emissions (not just locomotive exhaust) on the trace gas measurements?*

The train has a diesel engine. We use measured CO to identify periods sampling diesel exhaust, and have established a good correlation between CO and excess  $\text{CO}_2$ . On the northbound trip the sampling point is at the rear of the train, 700-900 m from the engine, but behind the locomotive and only a few carriages away on the southbound trip. We see no evidence for  $\text{CH}_4$  emissions from the diesel engine (no enhancements correlated with CO). We have not explicitly considered train emissions, but these would be expected to be small in comparison to the  $\text{CH}_4$  variability observed.

*P3736 L23-25: The  $\text{CH}_4$  mole fractions don’t show “three distinct regions” but their “behavior is distinctly different in three regions”. Small but significant variations in the south : : high variability north of 23 S. Are the “long pauses” at train stations? Why show the data at train stations or during stops downwind of cities when your discussion is focused on ecosystem influences?*

We have corrected the text accordingly and added a comment about urban emissions at Alice Springs, Katherine and Darwin. We prefer to show the entire data set and explain all the observed variability than selectively edit data from the record.

*P3737 L6: Which technology is “this technology” ?*

CCS – clarified in the text.

*P3737 L5-21: From my understanding, unlike all other measurement applications described in this manuscript, this section is not specific to the analyzer discussed in Section 2. Why does it appear in this paper? If you don't limit yourself to results obtained with the described analyzer you could potentially add every atmospheric measurement result obtained by FTIR. I don't think this section meets the objective of this paper.*

This study DID use the described FTIR analyser to measure both CO<sub>2</sub> and N<sub>2</sub>O simultaneously throughout the experiment, while both gases were released from the simulated leak. Both CO<sub>2</sub> and N<sub>2</sub>O were used to compare tomography results with and without significant background fluctuations of the trace gas concentrations (CO<sub>2</sub> is highly variable, N<sub>2</sub>O is not). I agree that the CO<sub>2</sub> measurements could have been made with a different analyser, but no other analyser was available capable of making the automated N<sub>2</sub>O measurements at the required precision on the same timescale. I have added this point to the text.

We are prepared to remove this example from the paper if it is felt to be too long – we leave it to the editor to decide.

*P3738 L1-4: Pertaining to my general comment (above) about sample drying, why here do you need one analyzer for water vapor analysis and another analyzer (sampling a dried air stream) for trace gas measurements? Could you do it all with one analyzer?*

See earlier comment on drying and cross-sensitivity to water vapour.

*P3738 L10-18: It appears (Figure 12) that at least the top sampling inlet (70 m) and likely others are above the nocturnal stable layer, so there should be no nighttime build-ups or depletions. Is this the case? You attribute the nighttime gradients to low turbulence in the canopy, but are there any connections between the surface and these upper sampling levels? And during daytime the PBL height must be greater than that of the canopy, so isn't there strong turbulence throughout the PBL and not just within the canopy?*

The 70m tower top level is ~ 30m above the canopy, and the site is not flat but in complex terrain at 1200m altitude near a ridge top. We generally do not expect a strongly stable nocturnal layer to form. However within the canopy there is often little or no wind or turbulence at night, leading to the observed strong vertical gradients from the 34 m level to the surface. Gradients in the top of the canopy and above it are weak. During day we agree the PBL is much higher and there is good mixing both within and above the canopy, leading to very small gradients both within and above the canopy. We have clarified the text to better reflect these comments.

*P3739 L2-6: It is unclear here what vertical scale length the flux gradient technique employs and how this scale length affects the minimum detectable flux values in Table 5. At what height(s) above the surface are measurements required to determine these minimum fluxes? The very brief description in this paragraph does little to help the reader understand the minimum detectable flux values in Table 5.*

We have added the Fick's Law equation and a vertical scale in the text ( 1m) and added further detail to the figure caption to explain the estimates more fully.

*P3739 L24: Here is a good example of over-extending the term "continuous measurements" - at "1 minute resolution or better". At what temporal resolution do measurements become "discontinuous"? Three lines below also claims "continuous".*

See previous comments on continuous measurements. I have added the term "averaging time" where appropriate.

*P3740 L7: Was the other system "applied" or "deployed" over a complete growth cycle?*

We have changed "applied" to "deployed".

*P3740 L28: ": : : because the \*respired\* CO<sub>2</sub> is depleted in <sup>13</sup>C."*

Corrected.

*P3741 L8: Are the <sup>15</sup>N isotopologues of N<sub>2</sub>O not "natural" like <sup>14</sup>N<sup>14</sup>N<sup>14</sup>O ?*

This paragraph has been substantially rewritten and Figure 16 removed.

*P3742 L6: ": : : and isotopic measurements \*of\* atmospheric trace gases."*

Done

*P3744 L24: "Hoffman" is misspelled here and in the text citation (P3719 L2)*

Corrected (sorry Dave).

*Tables 1 and 2 share common information including species, units, and GAW targets. Why not combine them?*

Good idea, we have combined tables 1 and 2.

*Figure 4: I'm a firm believer that Figure captions should explain all the symbols that appear in the graphs, so this caption needs to explain what the dashed lines mean.*

Agree. Done

*Figure 8: Are these measurements by FTIR or by other instruments?*

These are the FTIR data – the figure has been removed to reduce space, and Fig 9 (new Fig 8) now covers the whole 3 month campaign period.

*Figure 12: "represent measurement\*s\* at different heights : : :"*

Caption expanded and corrected

*Figure 14: There should be at least one horizontal line added to each panel as visual guide. These will help to show that background  $^{13}\text{CO}_2$  and  $\text{CH}_4$  were increasing over this period of seven sequential chamber closures. The behavior of several species in this plot is intriguing, yet the only description of this in the text is "complex". This comment very much pertains to my first general comment about overly brief descriptions of Figures.*

We have added horizontal axes to each panel. However more detail of the interpretation of the data in this plot, while we agree is interesting, is outside the scope of this paper, and will be described by the Qasom team. The data are shown here to illustrate the type of data available from the analyser.