**Response to Reviewers**
**Manuscript Number: AMT-2015-289**
**Manuscript Title: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor**

**The discussion below includes the complete text from the reviewer, along with our responses to the specific comments and the corresponding changes made to the revised manuscript.**

**All of the line numbers refer to the original manuscript.**

## Response to Reviewer #1 Comments:

This paper describes a two-channel broadband cavity enhanced absorption spectrometer for measuring important atmospheric trace gases from a research aircraft platform. This instrument clearly benefits from the authors' considerable experience in building and operating analogous cavity ringdown instruments on aircraft. They have thought carefully about engineering controls e.g thermal isolation/temperature control of the cavities, spectrometer and CCD. As a result, the instrument's mechanical stability is excellent – it is impressive how the authors are able to determine the cavities' mirror reflectivity from pressure dependent changes in Rayleigh scattering, without any mechanical deformation of the cavities. It is also impressive that measurements of water vapour made via its weak bands in the Ch455 channel agree well with data from a Picarro instrument. The instrument has been thoroughly characterised – the technical information in Table 1, the glyoxal wall losses in Table 2, and the lab & field detection limits in Table 3 will be helpful to other groups looking to build/refine their own BBCEAS systems. Preliminary data from flights over the US and China are very encouraging and demonstrate that the instrument performs (essentially) as well on the aircraft as it did in the lab.

**We thank the reviewer for the positive review and thoughtful comments. Listed below are our responses to the comments and the corresponding changes made to the revised manuscript.**

A significant technical advance with this instrument lies in how the authors have configured their single detection system to monitor two cavities operating in two different, neighbouring wavelength regions. I'd like to have seen more detail on (i) how the fibre optics that convey light from the Ch368 and Ch455 cavities are combined into the spectrometer (p11215 line 21 onwards);

**We have edited the text to clarify the CCD imaging:**

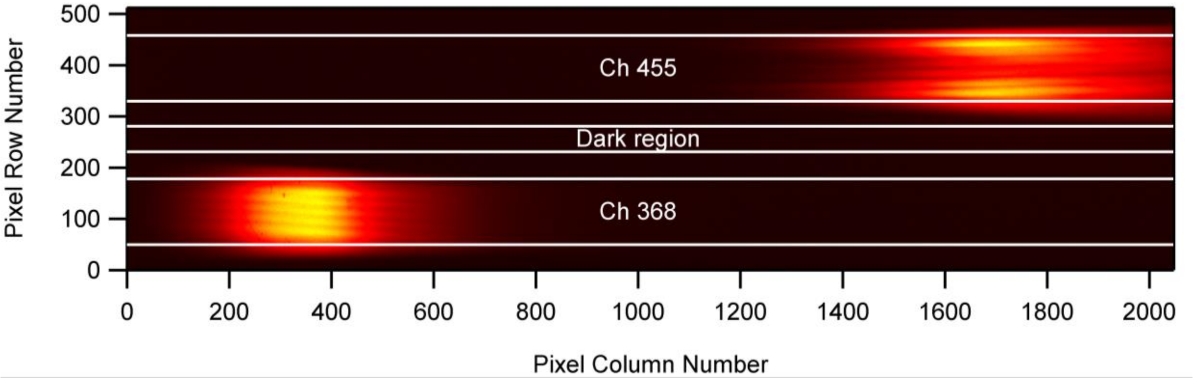
**Pg. 11215, line 27: "*Each BBCEAS channel illuminates one group of fibers, so that the light from the two channels is imaged onto two separated, vertical regions of the CCD detector.*"**

(ii) an extra figure showing a raw CCD spectrum and the "regions of interest" – is a single stripe illuminated on the CCD, spanning 119 nm, with information from the Ch368 cavity at one end and the Ch455 cavity at the other? (p 11216 lines 1-5);

**We have edited the text to clarify that we do not acquire the complete two-dimensional CCD signal, but rather record the accumulated signal for each spectral region:**

**Pg. 11216, line 12: "*While the LEDs are dark, the accumulated charge for the three spectral regions is sequentially transferred to the CCD readout amplifier and analog-to-digital converter, resulting in three separate spectra representing the vertically integrated counts for each region.*"**

**The figure below shows a full readout of the CCD, although this is not how the instrument is normally operated. It is possible to see the images of the individual fibers which are imaged onto the CCD. This spectrum was acquired in 0.4 s and shows the two illuminated regions of the CCD (each defined as 128 rows), and the dark region in the center of the CCD (defined as 50 rows). Each of the three regions span the full 2048 columns. When data is acquired during normal operation, we sum the column counts within each spectral region.**



(iii) an extra figure showing the electrical modulation scheme applied to the LEDs (line 10) and how that modulation links to the information recorded on the CCD.

**The electrical modulation of the LEDs is a simple square-wave function. Charge accumulates on the CCD when the LEDs are on and it is illuminated. Charge is read out from the CCD when the LEDs are off. We have clarified this in the text:**

**Pg. 11216, lines 6-10: "The CCD must be darkened while the accumulated charge is moved across the semi-conductor surface to a readout amplifier and analog-to-digital converter. This would typically be achieved using a mechanical shutter that requires ~8 ms to open and close, and can fail after rapid, continuous operation. To improve our instrument duty cycle and reliability, we electronically modulate the optical output of the LEDs *using a square-wave modulation, and read the CCD signal while the LEDs are dark*. *The LEDs are illuminated for 0.4 s, followed by 0.078 s when the LEDs are dark (0.006 s compensation time and 0.072 s CCD readout time), giving a total duty cycle of 84%.*"**

The introduction concisely makes the case for a glyoxal aircraft instrument in terms of addressing uncertainties in glyoxal's sources and sinks, and as a comparator for other (mainly remote sensing) glyoxal measurements. What comparisons can be made at this early stage between the glyoxal concentrations observed on flights over the central US or Beijing with, for example, satellite retrievals of glyoxal? I appreciate co-located satellite data might not (yet) exist; however do the glyoxal concentrations observed by BBCEAS broadly agree with those expected from previous satellite data? Can any similar comparisons be made for "hot-spot" methylglyoxal concentrations observed in the biomass burning plumes?

**The reviewer has raised excellent questions about the validation of satellite remote sensing observations using in situ measurements of glyoxal and methylglyoxal. Kaiser et al. (*2015*) considers the comparison of the aircraft measurements of glyoxal and formaldehyde, and their ratio, to satellite determinations over the southeast U.S. We refer the reviewer and interested readers to that reference. We are not aware of satellite retrievals of methylglyoxal, and the ACES instrument precision is not sufficient to retrieve this trace gas outside of biomass burning plumes and other large sources, so a meaningful comparison is not yet possible.**

Detailed/technical comments:

The abstract needs an extra phrase to explain that the light from the two cavity channels is dispersed by a single grating spectrometer and imaged onto a single CCD detector (P11211 line 5-6). It is also unclear what is "state-of-the-art" about the cavity mirrors (line 8) – exceptionally high reflectivity?

**We have changed the abstract:**

**Pg. 11211, lines 4-9: "The instrument spans 361–389 nm and 438–468 nm, using two light emitting diodes (LEDs) and a *single* grating spectrometer with a charge-coupled device (CCD) detector. Robust performance is achieved using a custom optical mounting system, high power LEDs with electronic on/off modulation, ~~state-of-the-art~~*high-reflectivity* cavity mirrors, and materials that minimize analyte surface losses.**

P11211 line 16-17: "BBCEAS is distinct from other techniques..., such as cavity ringdown spectroscopy (CRDS), because it employs a broadband light source and a multichannel detector." CEAS doesn't hold the monopoly on broadband cavity methods! CRDS has been demonstrated with various broadband lasers sources and multichannel detectors. See for example Chapter 3 in "Cavity Ring-down Spectroscopy – Techniques and Applications" edited G Berden & R Englen, John Wiley & Sons, 2009.

**The reviewer is correct and we have clarified this statement:**

**Pg. 11211, lines 16-17: "BBCEAS is distinct from other techniques in this class, such as cavity ring-down spectroscopy (CRDS), because it employs a*n unmodulated* broadband light source and a multichannel detector."**

Line 25-26. Adjust the phrasing. Currently the text implies N2O5 has a structured UVvis absorption band, whereas in practice N2O5 is detected via thermal conversion to NO3.

**We have edited the text:**

**Pg. 11211, lines 24-26: "Laboratory studies have used BBCEAS to measure a number of trace gases with structured absorption in the visible and ultraviolet spectral region, including $NO_2$, $NO_3$, $N_2O_5$ *(by thermal conversion to $NO_3$)*, HONO…"**

P11212 line 11. It's worth noting that aircraft measurements also provide vertical profiles of atmospheric species.

**We have edited the text:**

**Pg. 11212, lines 11-14: "Aircraft measurements of trace gases are important to satellite validation; *understanding vertical concentration profiles*; characterization of chemical lifetimes, processing, and transport; quantification of emissions and deposition; and the study of chemical mechanisms."**

P11213 after line 11. The introduction needs a few extra lines and references about the reasons for wanting to measure ambient methylglyoxal.

**We have added the following description of methylglyoxal:**

**Pg. 11213, lines 10-11: "*Methylglyoxal ($CH_3COCHO$) is a similar alpha-dicarbonyl species that may also be an important source of secondary organic aerosol mass (Kalberer et al., 2004; Lin et al., 2012). Global models indicate that the major source of methylglyoxal is isoprene (79%), followed by acetone (7%) and direct emissions (4%) (Fu et al., 2008).* The uncertainty in ~~both~~ the sources and sinks of glyoxal *and methylglyoxal* underscores the need for rapid, accurate, in situ measurements."**

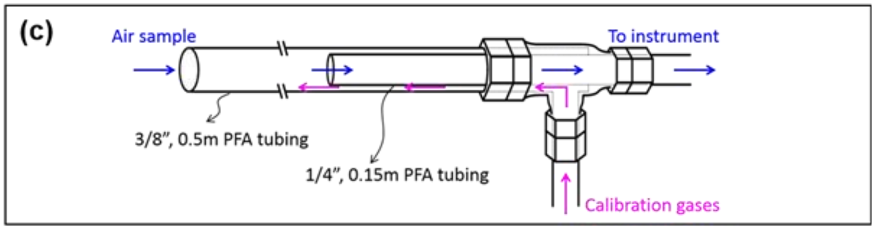
P11214 line 9 "This is the first instrument for in situ measurements of CHOCHO from an aircraft". The Volkamer group has published glyoxal measurements from an aircraft using a MAX-DOAS instrument [Atmos. Meas. Tech., 6, 719-739, 2013 and 8, 2121-2148, 2015]. The authors' claim of being first stretches a point. I guess it depends if one considers MAX-DOAS from aircraft to be "remote sensing" or "in situ" (there are also spatial averaging effects to consider when making "in situ" BBCEAS measurements on board a fast-moving aircraft).

**We understand and share the reviewer's concern about accurately representing the current state of aircraft glyoxal instruments, and our description is chosen carefully to differentiate the ACES instrument from what is already in the literature. We are not intending to overstate the novelty of our measurements. The MAX-DOAS method retrieves a slant-path averaged concentration, which is not normally considered to be an in situ measurement. We have edited the text to better highlight previous MAX-DOAS aircraft measurements:**

**Pg. 11213, lines 3-6: "Previously, remote sensing measurements of ambient glyoxal concentrations have been reported using long-path differential optical absorption spectroscopy (DOAS) *(Volkamer et al., 2005a; MacDonald et al., 2012)* and multi-axis DOAS (MAX-DOAS) ~~(Baidar et al., 2013)~~ *(Sinreich et al., 2007), including MAX-DOAS measurements from aircraft (Baidar et al., 2013; Volkamer et al., 2015)*."**

P11217 lines 8-17. I found it difficult to form a picture of the coaxial inlet from only the technical information given in the text. Would the authors consider providing a more detailed schematic of the coaxial inlet than that shown on the left of Fig 1b?

**We have modified Fig. 1 to add an additional panel:**



**We have edited the text:**

**Pg. 11217, lines 11-12: "The coaxial inlet consists of 0.95 cm OD tubing (0.35 m length, 0.79 cm ID), which contains 0.64 cm OD tubing (0.15 m length)*, as shown in Fig. 1c*. The 0.64 cm OD tubing runs through the PFA tee…"**

**Pg. 11243, Fig. 1 caption: "*(c) ACES inlet system, consisting of an outer Teflon FEP tube (0.95 cm O.D.; 0.79 cm I.D.; 0.5 m long) and coaxial inner Teflon FEP tube (0.64 cm O.D.; 0.15 m long). The coaxial design allows calibration gases to be added without affecting the inlet pressure.*"**

Line 23. The authors tested for "discontinuities in HONO before and after a filter change". Later on P11226 line 5-7 it says "We have minimised sampling artefacts... but have not characterised the inlet behaviour under different atmospheric conditions". Did they see any evidence for HONO production (or losses) on surfaces of their instrument or its inlet any point in their lab tests or field work?

**We did not see evidence for HONO production or loss on the inlet surface during our measurements, but we also did not conduct extensive laboratory tests with varying relative humidity and $NO_2$ for this inlet design. We have been careful to accurately represent this in the original text:**

**Pg. 11226, lines 1-7: “HONO inlet artifacts are more difficult to characterize, since HONO may undergo loss due to adsorption or production due to heterogeneous reaction of $NO_2$ and $H_2O$ (Finlayson-Pitts et al., 2003). The latter is of particular concern in assessing the accuracy low-level HONO mixing ratios during daytime (Li et al., 2014). For this work, we have minimized HONO sampling artifacts by using a short inlet with short residence time, but have not characterized the inlet behavior under different atmospheric conditions.”**

P11218 line 2. Can the authors provide more information about why the mirror purges were found to be unnecessary? Was this still true when operating in polluted regions (e.g. the China field site)?

**The reviewer has raised an important question. We have modified the text.**

**Pg. 11217, line 28 – Pg. 11218, line 4: “The mirror purges were found to be unnecessary *during SENEX, SONGNEX, and UBWOS, due to a combination of reduced cell pressure, aerosol filtration, and cell temperature (controlled at 30 °C)*, and their absence eliminates the small uncertainties from flow dilution and the relative sample length occupied by sample gas and purge gas over the length of the cavity. *During CARE Beijing-NCP, the mirrors required daily cleaning due to compromised reflectivity, likely due to high concentrations of organic species, high relative humidity, and high ambient temperatures.*”**

Line 17 “[Wall reactions on] flow system’s materials can...”

**We have corrected the text:**

**Pg. 11218, line 17: “*Surface reactions on f*~~F~~low system materials can potentially cause production or loss of target analytes, affecting the accuracy of in situ measurements.”**

Line 21. Thalman et al (Atmos. Meas. Tech., 8, 1835–1862, 2015) also tested for, and were able to exclude, heterogeneous production of glyoxal from ozone reactions on Teflon lines.

**We have added that information to the text:**

**Pg. 11218, lines 20-21: “Prior measurements have shown that inlet length has negligible impact on glyoxal losses for PTFE tubing (Huisman et al., 2008) *and that ozone addition to a Teflon inlet does not produce glyoxal or methylglyoxal (Thalman et al., 2015)*.”**

P11222 Why were measured reference spectra preferred when fitting for NO2 and glyoxal? What was inadequate about reference spectra generated by adapting literature absorption cross sections to the instrument’s line shape?

**We have added a brief discussion of the advantages and disadvantages of using measured reference spectra:**

**Pg. 11222, line 12: “*Measured reference spectra can be used to achieve more precise fits, because they are acquired with an identical instrument lineshape as the ambient measurements. However, it is necessary to carefully consider the accuracy of the measured reference spectra and the presence of trace gas contaminants, both of which may introduce errors into the spectral fitting.*”**

P11223 (and Fig 4 caption) First paragraph uses two different pressure units: hPa and mb.

**We have changed “mb” to “hPa”, and corrected this throughout the paper.**

P11225 line 2. “The Allan deviation in Ch455 is roughly 4 times smaller... due to the longer effective path length...”. Can this also be because the blue LED was brighter than the UV LED?

**We have edited the text:**

**Pg. 11225, lines 2-4: “The Allan deviation in Ch 455 is roughly four times smaller than Ch 368 up to 1 min averaging time due to the longer effective light path length *and greater LED intensity for* ~~of~~ Ch 455.”**

P11227 line 10. I appreciated what the authors were trying to achieve, but highlighting some of the data in bold in Fig 10 made these data look too noisy.

**We have changed Fig. 10 to remove the bold points.**

Line 16. The chemistry used in Roberts’ HONO source was first devised by Febo et al (Environ. Sci. Technol., 29, 2390–2395, 1995). Add the Febo reference.

**We have added the Febo et al. reference:**

**Pg. 11227, lines 15-16: “Constant HONO concentrations were generated using a calibration source based on the design by *Febo et al. (1995) and* ~~in~~ Roberts et al. (2010).”**

P11228 line 2. The fit errors for 5s HONO measurements are given as 314 pptv. However the 1.38 ppbv offset in Fig 10f suggests a somewhat larger systematic error.

**The reviewer has raised an important point. We have edited the text:**

**Pg. 11227, line 25 – Pg. 11228, line 1: “Fig. 10f shows the average and standard deviation of these additions, with high linearity ($r^2$=0.999). *The intercept value of -1.4 ppbv is greater than the observed precision of the measurements, and may be due to variability or inaccuracy in the HONO calibration source output.*”**

Line 18 onwards. It’s excellent to see co-measurements of NO2 by the new instrument and the NOAA group’s established CRDS instrument. But please quote the precision and accuracy for both instruments (using the same integration time).

**We have added this information to the text:**

**Pg. 11228, lines 19-21: “The CRDS instrument reported $NO_2$ concentrations at 1 s time resolution *with accuracy of 5% and 2-$\sigma$* precision ~~and accuracy~~ of ~~200~~ *60* pptv *(equivalent to 27 pptv for 5 s) (Wild et al., 2014)* ~~and 5%, respectively~~.”**

P11229 line 12. Consider re-phrasing: “NO2 and HONO concentrations peaked at night <give concentrations>, whereas glyoxal peaked during the day <give concentration>. Line 13 “NO2 and HONO mixing ratios were low during daytime and higher during nighttime, consistent with....” [add] “and NO2 and HONO photolysis during the day”.

**We have edited this paragraph:**

**Pg. 11229, lines 12-16: “*$NO_2$ and HONO concentrations peaked at night (65 and 3.5 ppbv, respectively), while glyoxal peaked during the day (240 pptv).* $NO_2$ and HONO mixing ratios were low during daytime and higher during nighttime, consistent with accumulation of $NO_x$ emissions in a shallow nocturnal boundary layer*,* ~~and~~ heterogeneous conversion of $NO_2$ to HONO on the ground surface*, and photolysis of $NO_2$ and HONO during the day*.”**

P11230 line 20. The projected HONO sensitivities achievable by longer averaging (100 pptv in 10 min and 40 pptv in 1 hour) aren’t supported by the Allan plot in Figure 8. This plot shows instrument stability limits the averaging times to between 1 and 5 mins (maximum).

**The reviewer is correct that longer averaging periods will require zero measurements to eliminate the instrument drift. We edited the text:**

**Pg. 11230, lines 18-21: "Due to its lower precision, the ACES HONO measurement in its current configuration is better suited to ground based sampling (e.g., 300 pptv in 1 min, 100 pptv in 10 min, 40 pptv in 1 h*, with long-term drift eliminated by zeroing*) and laboratory kinetic studies."**

Line 21. What is currently limiting the instrument sensitivity in the HONO channel – path length or photon counts? I agree better (ie more reflective) mirrors will increase the effective path length, but they won't necessarily lead to better sensitivity because better mirrors will also reduce the cavity output's intensity.

**In order for increased reflectivity to improve the detection limit, the cavity mirrors must have sufficiently low absorption and scattering losses. We have clarified this in the text:**

**Pg. 11230, line 21: "In the future, higher sensitivity could be achieved through higher quality cavity mirrors *with lower absorption and scattering losses in the coating* or different UV light sources that better ~~sample~~ *match* ~~its~~ *HONO's* strong absorption bands."**

P11246 / Fig 4. It's interesting the wavelength dependent loss for the UV cavity is not a smooth curve (Fig 4a), but has a pronounced and reproducible "bump" around 367 nm. This is worth noting; it also illustrates the strength of the method used here to determine the mirror reflectivity – many other groups would assume the reflectivity curve is a simple U-shape.

**We agree with the reviewer our direct measurements of the mirror reflectivity across the entire wavelength region of interest are more accurate than scaled, single-wavelength measurements or other approximations.**

P11247 / Fig 5. Should the green line in the top left panel be dashed?

**We have changed Fig. 5 so that the green line in the top left panel is dashed.**

P11248 / Fig 6. I was confused by the "i" in the top left of each panel. Also I didn't see the need to reproduce the measured spectrum in every panel, especially when the target absorber makes only a very small contribution to the spectrum. Likewise for Fig 7 for both comments.

**We have eliminated the "i: " text in Figures 6 and 7. Our goal in reproducing the measured spectrum in each panel is to show the contribution of the target absorber to the total, which is small in some cases.**

P11250 / Fig 8. Why are the Allan plots generated from photon counts in a single pixel rather than from retrieved HONO and NO2 concentrations? What are the dashed lines either side of the dotted line for random noise?

**We have chosen to report the Allan deviation in units of cm$^{-1}$ to allow a direct comparison of the ACES performance with existing different cavity enhanced instruments. We have clarified the text:**

**Pg. 11225, line 1: "*The precision for individual pixels, rather than retrieved gas concentrations, allows the instrumental performance to be directly compared to other cavity enhanced instruments.*"**

**We have removed the dashed lines from the Allan deviation plot in Fig. 8.**

P11252 / Fig 10. Personally, I thought figs 10a and 10d were too crowded. I'd show NO2 time series measured by the Ch368 and Ch455 channels on separate plots (Fig 10a). I also found it difficult to discern between the two scatter plots and best fit lines in Fig 10d.

**We appreciate the reviewer's concerns that Fig. 10 contains a large amount of information, but we prefer to display the Ch 368 and Ch 455 $NO_2$ data in the same panel for comparison.**

P11253 / Fig 11. The flight track in 11(a) is almost entirely blue and green. Is it possible to adjust the colour scale to show more information? The CHOCHO vertical scale in 11(c) has two zeros. In the figure caption, state whether the CRDS NO2 data has been moved up or down by 1 ppbv in 11(b).

**We have changed the color scale in Fig. 11a to better show the glyoxal concentrations.**

**We have corrected the y-axis for Fig. 11c. We have edited the caption:**

**Pg. 11253, Fig. 11 caption: "$NO_2$ measured by CRDS is ~~offset~~ *decreased* by 1 ppbv for clarity."**