

Interactive comment on “A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor” by K.-E. Min et al.

Anonymous Referee #1

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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 me-

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chanical 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.

Comments:

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); (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); (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 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?

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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?

P11211 line 16-17: “BBCEAS is distinct from other techniques..., such as cavity ring-down 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.

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

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

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

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).

P11217 lines 8-17. I found it difficult to form a picture of the coaxial inlet from only the

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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?

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?

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)?

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

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.

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?

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

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?

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.

Line 16. The chemistry used in Roberts’ HONO source was first devised by Febo et al

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(Environ. Sci. Technol., 29, 2390–2395, 1995). Add the Febo reference.

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.

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).

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".

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).

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.

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.

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

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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.

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?

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.

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).

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 11209, 2015.

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