Instrument inter-comparison of glyoxal, methyl glyoxal and NO$_2$ under simulated atmospheric conditions

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Response to Referee: Thomas Hanisco

This paper describes the results of several experiments in two different atmospheric simulation chambers that use several instrument using similar and different techniques. The measurements of Glyoxal and Methyl Glyoxal are examined from a standpoint of validating the measurements and the techniques. The paper is mostly well written and suitable for AMT. The work addresses an important scientific problem and provides use data and interpretations. The methods are sound and the work is novel. The study is especially thorough for high concentrations of Glyoxal, at least, and provides conclusions that will be useful to the AMT readership. This paper should be published with minor revisions.

General comments/question:
1) This paper examines the accuracy and precision of Glyoxal and methy glyoxal at simulated ideal conditions. The relevance to the atmosphere needs to be discussed a bit more in the conclusions. From my perspective, you did a great job of validating the cross sections for DOAS and the impact of NO2. I think this is the major point of the paper. What you have not shown as clearly is how measurements at these relatively high concentrations translate into measurements at 50 ppt in the real atmosphere. When I look at Figure 3 near the intercept, I can't help but think that there might be a very different set of results for an experiment that covers only the 0 – 100 pptv range. Do you expect these DOAS instruments to agree so well at 50 ppt? Is the absence of NO$_2$ interference still true when CHOCHO is only 50 ppt? A few sentences or a paragraph would be useful to me to help me understand how to connect the accuracy in these experiments to the real world measurements.

We have added a separate Section 4.6 to the discussion of ambient glyoxal concentrations (mostly below 300 pptv, and below 500 pptv in all cases), and their NOx dependence. Glyoxal is mostly a biogenic gas, and NOx levels in biogenic regions rarely exceed a few ppbv. In urban hotspots glyoxal concentrations are often higher, and even here NOx rarely exceeds few 10 ppbv. Over oceans the concentrations can be as low as the reviewer suggests, but there is very low NO$_2$ in these environments. We have added a separate Table 5 with correlations of these low concentration periods, and separately evaluated periods in the absence and presence of NO$_x$.

2) How do sampling artifacts affect these measurements? In general are these not a concern with CHOCHO? It seems to me that some of the measurement issues, especially with MAD-LIP are problems with implementation rather than issues that are inherent to the technique (Sec 4.2). Along these lines, might better results have been obtained under better circumstances for the Madison team? I don't believe that the DOAS instruments "benefit from direct calibration" nor do I think MAD-LIP suffers from not having what you consider a direct calibration.

The new discussion of the low concentration data in Section 4.6 and Table 5 provides further insights into issues with sampling glyoxal at low concentrations. It is true that some of the issues discovered with the Mad-LIP data are issues of implementation. Others, such as the cross-talk in methyl glyoxal if glyoxal is present, are more fundamental.

What this sentence refers to is that the need for external calibration always adds another source of uncertainty. We have modified the text in Section 4.2 and now refer to 'absorption techniques' rather than 'instruments that benefit from direct calibrations'. Uncertainties introduced from the need for secondary calibration sources are not unique to the measurements presented in this manuscript. See for example Table 1 in Schlosser et al., 2009.

Schlosser et al., Technical Note: Formal blind intercomparison of OH measurements: results from the international campaign HOxComp, *Atmospheric chemistry and physics,* **9,** 7923 - 7948 (2009)

Equation 1 (and following paragraph): The slant column usually refers to the atmospheric column. Just "column density" would be more appropriate.

Slant Column Density is a commonly used term in the DOAS literature to denote level 1 data (the output from the DOAS fitting). Technically photons do not travel on parallel paths to the cavity axis either. We prefer to keep this term, as it distinguishes level 0 data (spectra) from 2 data (volume mixing ratios) .

Section 2.1.6 (Description of Mad-LIP instrument): This section is too long and detailed. Why not just reference the instrument papers for this and the other instrument sections???

The ring down cell description is relevant because the Mad-LIP team had rearranged the design of the cell from previous experiments. It has not been described in this detail previously. The methyl glyoxal bit should stay since the Mad-LIP team has not published that method of methyl glyoxal determination before. Aside from these two parts, there isn't much left to cut out aside from a basic description of the instrument in order to explain the methyl glyoxal part. While this section is quite long, we wanted to include sufficient enough detail to make the manuscript fairly self-contained and allow for the description of anything in the analysis that varied from previous/other deployments that were unique to these specific conditions.

Page 8602 line 5 (Section 3.1): This looks like a significant offset in the PTR. Is there a sampling issue?

There is some sampling background for methyl glyoxal in this instrument and this is clear in the plots. This could be from contamination in the tubing from methyl glyoxal or other compounds that are detected at the same m/z. This was observed in many of the experiments on the chamber with this particular instrument and shows up as we would begin to sample from the chamber. This does not impact our discussion of the instrument correlations for methyl glyoxal response (slope) but does influence the observed offset.

Page 8602 line 23: Is this 33% for the supplement or for Figure 3?

This 33% refers to the variability of all of the experiments (as expressed in the previous line of variations in the slope of 0.76 to 1.09) as displayed in Table 3.

Page 8603 line 1: What do you mean scalable bias?

This was intended to mean that there is no linear function that adequately describes the bias. This has been changed to read: "and found minimal bias due to NO₂."

Page 8603 line 17: It does not seem obvious that this should scale. Have you made any measurements at lower CHOCHO with NO2?

This sentence has been reworded to state that the maximum relative interference would be 1 pptv of glyoxal/ppbv of NO_2.

Page 8611 line 13 (And references): This is a reference to the NASA instrument.

This reference has been updated to the Cazorla et al. 2015 reference for the NASA LIF instrument.

Page 8612 line 8: Replace "instruments which benefit from direct calibration" with "the absorption measurements"

We adopt the change suggested by the reviewer. We also note that the description "direct" is still accurate. Mad-LIP and SPME are instruments that have two calibration steps, each reference in a secondary manner to the absorption cross-sections (through ring-down or the chamber absorption measurements). The absorption measurements are more "direct" than techniques that require additional steps for quantification.

Page 8616 lines 8-11: This is misleading. I looked at the Coburn reference expecting a 1 Hz CE-DOAS measurement. It looks like the sampling is at 3 Hz and the signal averaging is still minutes or more.

There is nothing misleading here, as Coburn et al., 2014 indeed describes 2Hz glyoxal measurements. Signal averaging in 10 – 30 min intervals is needed for Eddy Covariance Flux measurements in order to sample a representative distribution of Eddies in the atmosphere.