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Atmospheric Measurement Techniques Discussions

Interactive comment on "Instrument inter-comparison of glyoxal, methyl glyoxal and NO_2 under simulated atmospheric conditions" *by* R. Thalman et al.

Anonymous Referee #3

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The authors present here a unique dataset of two intercomparison measurements at atmospheric simulation chambers, one at EUPHORE and the second one at NCAR. The measurements of glyoxal, methyl glyoxal and NO2 with a large range of instruments are the largest intercomarison for these instruments so far. It is an important research topic for the scientific community and thus this manuscript is a very valuable result for the scientific community. Indeed such manuscripts are typically long and difficult to read, as they contain a lot of information and aspects. But the authors made a good structure and separation in subsections. The manuscripts fits perfect to the scope of AMT. I have several aspects which I think are not addressed sufficiently or

not absolute correct. I recommend publication after correction and improvement of the manuscript.

Mayor points: In the manuscript extensive comparison of the measurement results is performed. But I agree with the Comment from Thomas Hanisco, that the investigation of measurement accuracy at atmospheric levels (e.g. glyoxal at 50ppt) is coming to short. In the conclusion even the impression arises that accuracy for glyoxal is sufficient good. These concentration ranges should be addressed in more detail. Also a more critical statement on the problems, especially in the conclusion, would be very useful. This would not degrade the work from the authors. In the UV/ VIS spectral range where glyoxal and methyl glyoxal are evaluated, overlapping absorption of water is present. The available spectra data from HITRAN have large uncertainties in this spectral range and large corrections were applied to the HITRAN H2O absorption cross section in this spectral range for the different HITRAN data products. It is unclear to me why this mayor issue for the glyoxal and methyl glyoxal spectral data evaluation is not investigated in much more detail during this study. I understand that this is now not possible, but it should be stated in the Abstract, Section3.2.4 and the conclusion, that during this study the effect of H2O on the UV / VIS absorption measurement of glyoxal and methyl glyoxal was not investigated systematically and in more detail and thus no clear conclusion on the influence of H2O absorption can be made.

More specific points: p. 8583 l.28: “For glyoxal and methyl glyoxal the slopes varied by less than 12% and 17% (both 3-sigma) between inherently calibrated instruments (i.e., calibration from knowledge of the absorption cross-section).” I do not understand what you mean with 3-sigma for a slope. The slope is the slope of the linear correlation fit. What does than the 3-sigma mean?

p. 8587 l. 17: “R=0.999972” is it the measured reflectivity? Is it the peak of reflectivity? To which peak absorption path does it relate in air/ vacuum under your measurement conditions?

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p. 8588 l. 6: “empty cavity”: what do you mean with empty? Vacuum?

p. 8588 Eq. (1): The absorption path L(lamda) vary with wavelength lamda, Also absorption cross sections vary with wavelength (this should be added). But the right side of the equation using the O4 SCD does not depend on wavelength. So this equation is in that way not correct. It is just an approximation for the wavelength where you evaluate the O4 absorption.

p. 8588 l. 21: “. . .and perform DOAS fitting of multiple reference spectra simultaneously. Literature absorption cross-sections for glyoxal (Volkamer et al., 2005b), methyl glyoxal (Meller et al., 1991), NO2 (Vandaele et al., 2002), and O4 (Hermans et al., 1999; Hermans, 2010) were used in fitting the spectra.” – As it is written in other sections, I understand that the same literature absorption cross sections are used for the different instruments. Is this correct? But this is the only definition of reference spectra. It is not obvious from this section that the same references from here are used for the different instruments. Also H2O is not included here for the experiment with higher RH. I suggest making clear which instrument uses which reference spectra (e.g. in Table 1).

p. 8588 l. 21: “The DOAS output in units of slant column density (SCD=concentration âĂć L) was then divided by the path length to get concentration.” – But the absorption path length depends on the wavelength. I can somehow follow how the analysis was done, but the way it is written, it is not clear.

p. 8588 l. 21: “Equation (1) was solved iteratively to account for self-limitation until the concentrations converge (either for NO2 (experiments 3, 4, 7, 9 and 10) or glyoxal (exp 1 and 8)).” – Why it should converge differently for NO2 and glyoxal? The physical principle is the same.

p. 8589 l. 16: “LED peaking around 455nm” – Is the LED intensity stabilized (e.g. with temperature stabilization). The BB-CEAS data analysis algorithm relies on a stable intensity of the light source. Any intensity variation directly scales the observed

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concentrations and thus significantly increases the measurement error. This cannot be observed in measurements without absorber (zero drift experiments like shown in Fig 9 and 10).

p. 8589 l. 18: “peak reflectivity= 0.999817 at 462 nm“ – measured? To which peak absorption path does it relate in air/ vacuum under your measurement condition.

p. 8590 l. 9: “typically 6th order” – This is very high for a spectral analysis and cannot be explained by the aerosol absorption. Only the missing ozone absorption could explain it (as stated later). Also other instrument issues could cause such problems. Thus clarify this already here.

p. 8590 l. 14: “instrument’s spectral resolution (between 0.09 and 0.13nm half width at half maximum)“. This high spectral resolution with this spectrometer indicate an under sampling of the instrument function (min. 5 to 10 channels). Even if a used asymmetric line shape function is derived from 20 lines this is problematic, as the line shape function is changing significantly over the spectral range of the applied spectrometer. Thus not necessary the “real” line shape function for the fitting window is derived. Is this error source evaluated?

p. 8590 l. 14: “The instrument was subject to small long-term drifts over the _12 h duration of the Allan tests that degraded the achievable precision.” Alan test at zero concentration does not show errors due to intensity drift of the light source, as this will be in BB-CEAS a scaling of the derived concentration. But if concentration is zero, no scaling effect will be visible.

p. 8591 l. 15: “The overall accuracy of the BBCEAS concentration measurements is estimated to be 7% for glyoxal and NO2 and 10% for methyl glyoxal.“ – The noise in the spectrum will be the dominant error source at very low concentrations. It defines a minimum error for the measured components. Thus an error in percent is not absolute correct as it would give a much better accuracy for very low concentrations, than the correct value.

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p. 8592 l. 11: “using dry nitrogen as a carrier“ – Is it comparable to the measurements?

p. 8592 l. 18: “tuning on the scale of the vibro-rotational absorption spectral features of glyoxal ($\sim$0.06 nm)” - At which wavelength? What is the phosphorescence wavelength? Please clarify this at the beginning of the instrument description. This would also be useful to understand the different filters on p. 8593. It is often not clear if you mean the laser light or the phosphorescence light.

p. 8593 l. 1: “The variability of the alignment is reflected in variability of the calibration factors.“ – Pleae clarify. The misalignment should not change the absorption path in a white cell. So is this just an intensity variability which would require a new calibration?

p. 8602 l. 16: “It should be noted that the W-DOAS instrument is affected by the distortion of the light beam during the flushing of the chamber“ – How should a distortion of the light beam affect the correlation? The distortion should reduce light intensity but not the absorption path and thus only slightly increase the measurement error, but not the value itself.

p. 8603 l. 14: “Deviations in the SPME concentrations were large but appear to be unconnected to the high NO2 levels in the chamber. For both CE-DOAS and BBCEAS (Fig. 4) we do not find significant bias, i.e., an upper limit change in glyoxal due to NO2 is derived as $\pm$200 pptv glyoxal in the presence of 200 ppbv NO2 (or 1 pptv glyoxal/1 ppbv NO2).” – I cannot follow this conclusion. I think the plot S5 show a clear connection of glyoxal with NO2. I think this is an important analysis and should be part of the main paper. A bias of 200ppt for glyoxal would be a significant value for atmospheric concentrations.

p. 8604 l. 12: “before and after HONO addition“ – The structure of this section is very confusing. Why the addition of HONO is mentioned not at the beginning when the experiment is explained?

p. 8604 l. 28: “However, the variations in slopes were somewhat higher, i.e., 0.94–1.54

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(glyoxal), and 0.7–2.2 (methyl glyoxal), while most instruments agreed within 30% for both species (see Table 3).“ - If variation is so high, could you provide a plot in the manuscript?

p. 8605 l. 26: “The RH varied between 45% and 58 %” - First of all this variation is very small to investigate an interference. Second, for the spectral interference not RH but concentration is important. Third, it is not clear to me how from the performed measurements an influence of water on the measurement of glyoxal and methyl glyoxal should be observed. And this should actually be done for concentrations which are typical in the atmosphere. I cannot see how an influence in the range of 100ppt for glyoxal can be excluded from the presented measurements just by the intercomparison of the different instruments at typically much higher concentrations. So how the authors derived the influence of water absorption? Why is there no W-DOAS data for this experiment?

p. 8606 l. 1: “The slopes of correlations (Table 3) varied between 0.95–1.5 (glyoxal), 0.68–1.83 (methyl glyoxal),. . .” - This strong variability may indicate serious issues. It is linked to the question above.

p. 8606 l. 16: “Interference from O3” - This title seems to be confusing as not measurement interference directly due to ozone is investigated but rather the glyoxal production due to ozone. A second point to this chapter: You investigate mainly glyoxal production from ozone in Teflon tubing. But one of the mayor issue people worry is glyoxal loss in lines, walls filters etc. especially if they get wet. Why this is not further investigated? The authors themselves used heated sampling lines before to avoid such losses.

p. 8606 l. 16: “CE-DOAS and BBCEAS instruments changed the lengths of their sampling lines to attempt to observe any change in the measured concentration.” - Are these all new clean teflon lines? Can this be adapted to teflon lines used e.g. for few days at ambient conditions?

p. 8607 l. 17: “Fig S2” – This seems to be a rather important data set and should

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be part of the main manuscript. Fig 9 and Fig 10 could be moved to the supplement materials.

p. 8609 l. 6: “Direct comparison of the EUPHORE and NCAR IR spectra showed a factor of 0.78 difference, which was traced to a near identical correction factor that had previously been applied to the EUPHORE-IR spectrum (see Sect. 2.1.8).” – I could not find in the section 2.1.8 any explanation about this scaling factor. It is also not clear to me how this scaling can be explained. Please explain or give according references.

p. 8609 l. 21: “in slopes between PTR-ToF-MS and CE-DOAS of 0.95±0.03; this is essentially unity at the 95% confidence level.“ – The subordinate clause >this is essentially unity at the 95% confidence level< is obvious if you define your confidence level in such a way. Thus it is confusing and should be removed.

p. 8610 l. 5: “LOD=3 âĂć 1-Sigma variability+background” – what do you mean with background? It is unclear what value you are describing.

p. 8610 l. 15 “Any deviation from pure white-noise residuals can be accessed from multi-channel sensors, and provides additional information to assess LOD from a perspective of “accuracy”.” – Also the size of the white noise give additional information to access the LOD.

p. 8610 l. 20 “We used Eq. (7) to calculate experimental LODs using the 1-sigma variability of data from the overnight dilution experiment on 5–6 July 2011 (E8b; see Fig. S2 in the Supplement).“ – But this method ignores systematic offsets of an instrument what clearly increases the LOD. Thus the calculated LODs are too optimistic, as offsets can clearly be observed already without interfering gases in Fig. 9 and 10. At least these offsets should be included and influences from other interfering gases on LOD should clearly be pointed out.

p. 8610 l. 23 “listed together with LOD values submitted with their measurement data by the operators of the various instruments.” – Are the operators derived LOD are

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calculated in the same way?

p. 8611 l- 19: “from the overnight dilution experiment” – Provide also experiment number from Table 3.

p. 8614 l- 15: You start here explaining a different experiment. However this I not clear in this chapter. I suggest rephrasing the sentence to make it clear to the reader.

p. 8614 l- 26: “bias due to NO2 as ca. 1 pptv glyoxal/ppbv NO2 (Fig. 4) and 5 pptv methyl glyoxal/ppbv NO2” – How these two values derived from the plot? Please be more specific.

p. 8615 l- 7: “The combined effect is a decrease of a factor of 16 in sensitivity.” – This seems not to be correct. The loss in sensitivity due to the loss in light is only sqrt(4) = 2, and the loss due to the reduction in light path is $\sim$4. Thus the total loss in sensitivity is 2x4=8.

p. 8616 l- 1: “Alpha-dicarbonyl” – I suggest to use glyoxal and methyl glyoxal to be more systematic in the manuscript and not to confuse the reader who is often not familiar with the name of Alpha-dicarbonyl.

p. 8616 l. 3: “detection of glyoxal at ambient mixing ratios in urban, semi-polluted, biogenic, arctic and marine environments. In most urban environments the glyoxal detection by in situ UV-vis absorption techniques is feasible,..” – Please be more specific. What are typ. concentrations observed in these areas. How do the concentrations in this study relate to these concentrations? From the given data it is not obvious that the instrumentation is feasible to measure these concentrations as your comparison is mainly at high concentrations. Also a detailed analysis of water interference was not performed.

p. 8617 l.1: The conclusion should be critical. It should of course state what was done, what is working etc. But it should also point out where still significant problems are, what should be done to minimize problems and which investigations are still needed.

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The statements sound like there are mainly no major issues for the measurements. This can lead to misinterpretations. For example are the results of cross sensitivity not critical enough. They are maybe true for high glyoxal and methyl glyoxal values but not for very low values like typically present in the atmosphere. Also several experiments do not allow to give a clear statement like the observation with RH. So in each point of the conclusion it should be clearly stated for which conditions the specific conclusion is valid.

p. 8618 l. 21: "Future studies should further investigate in detail the effect of O3 and H2O at very low concentrations of Alpha-dicarbonyls (<20 pptv) and high relative humidity (>80% RH), when losses/formation of Alpha-dicarbonyls in sampling lines or to/from aerosol filters are likely to be more relevant." – How do you come up with the values of 20ppt and 80%RH? How can you conclude that this is not already a problem at higher concentrations?

Supplement l. 69: "... Mirror Reflectivity ($\pm$2%),..." – this would implement that the mirror reflectivity is measured with this accuracy. But how accurate is that measurement and how it is performed?

Supplement l. 81: "the fit error for the SCDgly is on the order of 15%..."- But here you do not recalibrate the light path like described in section 2.1.3. The measurement from O4 and the scaling would introduce an additional, not negligible, error source.

Supplement l. 83: ".. the fit error is 1.5- 2.0% over the full range of glyoxal concentrations investigated in absence of interfering species" – This makes no sense as you should have a minimum error due to the noise in the spectrum.

Supplement l. 119: "The overall uncertainty in the CE-DOAS calibration is 3.5%,..." – This error budget seems to miss the recalibration error from O4 (see above).

Table 3: Why experiment E9 is missing?

Table 4: Accuracy in % is not absolute clear. Please give reference to the section

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where a description of the calculation is given.

Fig. 1: Where is the FT-IR light path?

Fig. 2: Use same labels for the plots (small / capital letters). What do you mean with "Units of fit intercepts"? – The concentration? You use pressure and temperature of the camber to convert to pptv. But these values can be very different in the instruments outside the camber. Was this considered? The PTR-MS sees a clear step at 20:35 which was not seen by the other instruments. How this could be explained?

Fig. 3: The range below 300ppt is the most interesting, as typical ambient concentrations are below this value. However on this shown scale no information on this most relevant range is given. Even if several instruments have not sufficient accuracy, those who have could be plotted.

Fig. 4: Units for NO2 are missing. A clear correlation to NO2 is visible even if it is different for the different instruments. What is the implication for real atmospheric background levels of e.g. 50ppt?

Fig. S5: In figure A a clear dependency and trend for higher NO2 levels can be found, thus the sentence it the caption seems to be wrong.

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