

## ***Interactive comment on “Profiling of formaldehyde, glyoxal, methylglyoxal, and CO over the Amazon: Normalised excess mixing ratios and related emission factors in biomass burning plumes” by Flora Kluge et al.***

**Flora Kluge et al.**

flkluge@iup.uni-heidelberg.de

Received and published: 13 July 2020

The reviewers comments are written in **bold**, our responses are marked with AC (authors comments).

We are very grateful to the reviewer for his comments and overall very positive assessment of our manuscript, to which we react in the following way.

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Comments:

**Having this gap within the glyoxal fit window to avoid cross interferences with H<sub>2</sub>O is interesting. Would it be possible to better illustrate the impact of doing this (e.g. compare SCD with/without gap)? Why is not needed for the methylglyoxal fits?**

AC: In fact, we tested various fitting scenarios including/excluding the inferring water vapour absorption. When including it, the residual structure was dominated by the residual water vapour absorption, casting doubts on the fitting results for glyoxal. Accordingly, we discarded the retrieval including the water vapour absorption and decided for the spectral retrieval as shown in the manuscript. The same was not the case regarding the DOAS retrieval of methylglyoxal.

**In Fig. 8, there are some peaks in CO measurements to which no specific event is allocated and the other way around, there are biomass burning events without any increase in CO concentrations. Do we understand that? A similar comment can be done for other species. For example, in the fire event 2, a spike is visible in CH<sub>2</sub>O measurements but not in C<sub>2</sub>H<sub>2</sub>O<sub>2</sub> nor in C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>, while in the event 6, this is the reverse. Are those fires from different origins?**

AC: In lines 206 – 209 and 289-291, we argued that a direct comparison of in-situ and remotely sensed parameters is only useful on spatial scales larger than the spatial resolution of the remotely sensed parameters. Therefore, a missing one to one correlation (c.f. at 17:30 and at 18:15 for the HALO flight AC 11, fig. 8) between the various in situ and remotely sensed parameters is per se not astonishing. Also, CH<sub>2</sub>O absorption was measured in the UV spectral region, while C<sub>2</sub>H<sub>2</sub>O<sub>2</sub> and C<sub>3</sub>H<sub>4</sub>O<sub>2</sub><sup>\*</sup> were measured in the vis, using two different spectrometers which are not temporally aligned. Therefore, the differences in the temporal recording time of both spectrometers may cause different detection sensitivities for specific fire events. For example, the temporal resolution of the UV spectrometer was roughly four times lower than the temporal resolution of the

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vis spectrometer for event 2, during flight AC11 (fig.8). While it is possible that the in situ and remote instruments probed different airmasses, this is not possible for our remote sensing measurements, since the mini DOAS telescopes all point into the same direction (with the same field of view).

**In figure 9, in case the measurement sampling allows to do so, it would be very interesting to see mean concentration profiles classified as a function of the type of air mass (pristine, biogenic, fires, pollution).**

AC: This would indeed be interesting, but how to distinguish among the four situations without any further information. From the measured data the only criteria to discriminate among the different air masses could come from the measured concentrations and possibly air mass trajectories. We used both approaches in our study, but they may at best allow us to distinguish between pristine and biogenic emission affected air masses (i.e. the data belonging to the lower quartile) on one hand and on the other hand those affected by biomass burning and air pollution (all other elevated concentrations). However, we strongly feel that such a qualitative sorting may not provide robust information on the origin of the air masses and in consequence we refrain from it.

**During the discussion on the R<sub>GF</sub> and R<sub>mf</sub> profiles, I would be much more cautious as the level of noise is very high. I think that the only thing which can be said is that the ratio is lower in the boundary layer compared to higher altitudes. Other conclusions on the profile shape are quite hazardous.**

AC: The larger scatter of data in particular at larger altitudes when the concentrations are low may partly or even mostly be due to the detection limits of the respective gases (see fig. 4) and thus not express atmospheric variability. Therefore, we mostly concentrate our discussion on comparisons to other studies made at low altitudes. The paragraph in lines 485-494 has been rephrased to emphasize the high level of noise: "Finally, the vertical profile of  $R_{GF}^*$  indicates slightly elevated ratios above the boundary layer and in the free troposphere (fig. 12, panel b). Within the boundary layer,  $R_{GF}^*$

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remains approximately constant. Both features were previously observed by Kaiser et al., (2015) for altitudes up to 6 km, however less pronounced. The increase in  $R_{GF}^*$  between 2-10 km appears most pronounced just above the boundary layer (at about 2 km), where  $\text{CH}_2\text{O}$  and  $\text{C}_2\text{H}_2\text{O}_2$  mixing ratios are still significantly above the detection limits. Notably, the correlation of  $\text{CH}_2\text{O}$  and  $\text{C}_2\text{H}_2\text{O}_2$  is larger within the boundary layer than in the free troposphere. When discussing the profile shape of  $R_{GF}^*$ , one has to keep in mind the very low  $\text{CH}_2\text{O}$  and  $\text{C}_2\text{H}_2\text{O}_2$  mixing ratios in the upper troposphere and the increasing influence of measurement noise on the inferred mixing ratios. Above 6 km, we observe mean  $\text{CH}_2\text{O}$  and  $\text{C}_2\text{H}_2\text{O}_2$  of only  $54 \pm 40$  ppt and  $15 \pm 5$  ppt, respectively, and accordingly,  $R_{GF}^*$  varies on average by 60% among the different measurements within the same altitude range."

**When computing R<sub>xf</sub>, how do you define the background? Out of the different marked events (red, green, blue events), there is still a large variability in the measured concentrations with values sometimes as large as during the selected events. So the notion of background is unclear here. Please clarify this aspect.**

AC: For clarification of the background definition, lines 515-521 have been changed to: "Due to the lack of respective  $\text{C}_2\text{H}_2\text{O}_2$  and  $\text{C}_3\text{H}_4\text{O}_2$  measurements, we infer mean background mixing ratios  $[X]_{bkg}$  for all three gases by binning the data in 100 m altitude stacks and calculating the mean of the lower data quartile for each bin as displayed in fig. 9 (grey line). As fig. 10 shows for the case of formaldehyde, the such defined background mixing ratios approximately correspond to formaldehyde measurements of pristine air masses above the Western Pacific Ocean by Peters et al., (2012). In order to detect enhancements due to the plumes,  $[X]_{bkg}$  is then subtracted from the measured mixing ratios. From the resulting enhancements, the normalized excess mixing ratio..."

Minor/Technical comments:

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**Line 13: Correct “applaying” by “applying”**

AC: The typo has been corrected accordingly.

**Line 31: remove “is”**

AC: The text has been rephrased accordingly.

**Table 1 caption: write “Temperature” instead of “Temperatur”**

AC: The typo has been corrected accordingly.

**Line 162: add “transfer” after “radiative”**

AC: The text is rephrased accordingly.

**Line 177: replace “reminder” by remainder”**

AC: The typo has been corrected accordingly.

**Line 185: the statement “dominates with >50%” is not clear. Please rephrase.**

AC: The sentence in lines 193-195 has been changed to: “Up to 10 km altitude and for both investigated wavelengths, the absorption within the line of sight of the telescopes contributes with more than 50% to the total O<sub>4</sub> absorption. A relative minimum can be seen at the top of the planetary boundary layer. . .”

**Figures 2 and 3: All the different blueish curves tend to mix together. Please use more contrast colours to improve visibility.**

AC: The colors of the curves in fig. 2 and 3 are changed accordingly (see attachment).

**Lines 196-198: remove “on spatial scales. . .analysis of our data”, which is unclear.**

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AC: As outlined above, lines 206 – 209 and 289-291 describe why we refrain from directly comparing the in situ and remotely measured data. This seems important for the correct interpretation of fig. 8 as well as later in the manuscript, when inferring emission ratios with respect to formaldehyde instead of CO.

**Line 203: Uncapitalize “Fit”**

AC: “Fit” has been uncapitalized.

**Line 247: add “s” to “flight” (“flights”)**

AC: The text has been rephrased accordingly.

**Line 268: remove “in”**

AC: “in” has been removed.

**Line 269: replace “more closely” by “further”**

AC: The text has been rephrased accordingly.

**Figure 8: add a colour bar for R<sub>gf</sub>/R<sub>mf</sub>. Please mention in the caption what is the shaded blue area in the upper three panels.**

AC: The sentence “The shaded blue area in panels a to c shows the respective measurement uncertainty” has been added to the figure caption. The color coding of  $R_{GF}^*/R_{MF}^*$  has been removed as it did not provide any additional information.

**Line 313: remove either “are” or “appear”**

AC: The text has been rephrased accordingly.

**Line 335: this factor 2 is likely a very rough way to get C<sub>3</sub>H<sub>4</sub>O<sub>2</sub> concentrations since I suppose that the relative amounts of the C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>\* family members**

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**strongly depend on the precursor concentrations, and thus on the geolocation, altitude, geophysical regime. Please add a small statement to draw attention on this.**

AC: We accordingly added the following sentence in lines 349-351: "However, we note that the factor of  $2.0 \pm 0.5$  may largely depend on the precursor concentrations, and thus on the geolocation, altitude, and geophysical regime, and therefore barely provides more than a hint on its true size."

**Line 381 and figure 9 has as consequence that the basic assumption for error estimates is not verified (line 194). I agree however that some approximations are needed for such estimates. Please state when you make this hypothesis that it is not fully correct.**

AC: We agree and have accordingly changed the sentence in lines 210-211 to: "Summing-up all described uncertainties, the precision error of the combined methods can be approximately calculated according to eq. (1) as. . ."

**Section 5.3.1: Please mention the type of measurements that Kaiser et al. and MacDonald et al. have performed (altitude range, season, measurement type).**

AC: The text in lines 450-453 has been changed to: "The comparison with Kaiser et al., (2015) shows, that the inferred  $R_{GF}^*$  is notably larger than during most of their in situ measurements at altitudes ranging from the ground up to 6 km over the southeastern US in June-July 2013. Our results are in much better agreement with the  $R_{GF}^*$  inferred by MacDonald et al., (2012) from ground based DOAS measurements for altitudes between 0 and 1000 m over a southeast Asian tropical rainforest in April-July 2008."

**Line 444: replace "Contrary" before "On contrary"**

AC: The text has been rephrased accordingly.

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**Line 481: The sentence "As a result, ...burning plumes" is a repetition of the previous one to me. I suggest you delete it.**

AC: The sentence has been deleted.

**Line 570: replace "applaying" by "applying"**

AC: The typo has been corrected accordingly.

**Line 583: to my knowledge, there is very little direct emissions of HCHO from biogenic sources. It comes mostly from indirect production from other biogenically emitted VOCs such as isoprene.**

AC: The sentence in lines 607-608 has been changed to: "In the lower troposphere, enhanced formaldehyde mixing ratios have two major contributions: direct emission e.g. from biomass burning, and secondary formation during the degradation of short-lived VOCs, like isoprene."

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