

Authors point-by-point response to the referee comments RC1, RC2, and RC3 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.

We are very grateful to the reviewers for their comments and overall very positive assessments of our manuscript. In the following point-by-point response, the reviewers' comments are written in **bold**, our responses are marked with AC (authors' comments).

The document is structured as follows:

Pages 1-5: Reviewer Comment RC1

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Page 10-12: Reviewer Comment 12

Page 13-14: Additional changes in the manuscript by the authors

Reviewer Comment RC1:

Comments:

Having this gap within the glyoxal fit window to avoid cross interferences with H₂O 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 interfering 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 CH₂O measurements but not in C₂H₂O₂ nor in C₃H₄O₂, while in the event 6, this is the reverse. Are those fires from different origins?

AC: In lines 208 – 214 and 294-296, we argue 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_2O absorption was measured in the UV spectral region, while $\text{C}_2\text{H}_2\text{O}_2$ and $\text{C}_3\text{H}_4\text{O}_2^*$ 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 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 Rgf and Rmf 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 494-506 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}^* 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 CH_2O and $\text{C}_2\text{H}_2\text{O}_2$ mixing ratios are still significantly above the detection limits. Notably, the correlation of CH_2O 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 CH_2O 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 CH_2O and $\text{C}_2\text{H}_2\text{O}_2$ of only 54 ± 40 ppt and 15 ± 5 ppt, respectively, and accordingly, R_{GF}^* varies on average by 60% among the different measurements within the same altitude range.”

When computing Rxf, 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 529-535 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:

Line 13: Correct “applaying” by “applying”

AC: The typo has been corrected accordingly (line 14).

Line 31: remove “is”

AC: The text has been rephrased accordingly (line 32).

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 172).

Line 177: replace “reminder” by remainder”

AC: The typo has been corrected accordingly (line 189).

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

AC: The sentence in lines 197-199 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_4 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 have been changed accordingly.

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

AC: As outlined above, lines 208–214 and 294-296 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 220).

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

AC: The text has been rephrased accordingly (line 264).

Line 268: remove “in”

AC: “in” has been removed (line 285).

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

AC: The text has been rephrased accordingly (line 286).

Figure 8: add a colour bar for R_{gf}/R_{mf} . Please mention in the caption what is the shaded blue area in the upper three panels.

AC: The color coding of R_{GF}^*/R_{MF}^* has been removed as it did not provide any additional information. The sentence

“The shaded blue area in panels a to c shows the respective measurement uncertainty.”

has been added to the figure caption.

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

AC: The text has been rephrased accordingly (line 330).

Line 335: this factor 2 is likely a very rough way to get $C_3H_4O_2$ concentrations since I suppose that the relative amounts of the $C_3H_4O_2^*$ family members 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 355-356:

“However, we note that the factor of 2.0 ± 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 215-216 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 458-462 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 (line 475).

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 505).

Line 570: replace “applaying” by “applying”

AC: The typo has been corrected accordingly (line 609).

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 622-624 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.”

Reviewer Comment RC2:

Comments:

Line 10: The authors have not yet introduced RGF or RMF, and unless readers are already familiar with the chemical formulas for glyoxal and methylglyoxal, this may be confusing. I suggest either noting the names of the species in Line 1, or defining RGF and RMF here.

AC: We agree and have changed lines 1-4 to:

“We report on airborne measurements of tropospheric mixing ratios and vertical profiles of formaldehyde (CH_2O), glyoxal ($\text{C}_2\text{H}_2\text{O}_2$), methylglyoxal and higher carbonyls ($\text{C}_3\text{H}_4\text{O}_2^*$) (see below), and carbon monoxide (CO) over the Amazon Basin during the ACRIDICON-CHUVA campaign from the German High Altitude and Long-range research aircraft (HALO) in fall 2014.”

Additionally, in lines 11 and 13 has been added:

“The mean glyoxal to formaldehyde ratio R_{GF} ... The mean methylglyoxal to formaldehyde ratio R_{MF} ...”

Line 29: The authors state that these compounds are emitted, but much of the paper discusses their formation mechanism, so I would change “emitted” to “emitted or formed”.

AC: Line 30 has been rephrased to:

“Among the manifold of species emitted in large amounts by fires or formed in their plumes are carbonyl compounds...”

Line 52: The line “glyoxal and methylglyoxal are formed by 47% and 79%, respectively” is slightly confusing. Does this mean 47% of the glyoxal is formed from isoprene? Or 47% of the isoprene that reacts forms glyoxal?

AC: Yes, 47% of the total atmospheric glyoxal is formed from isoprene oxidation. To clarify this, the sentence in lines 54-56 has been changed to:

“Similar to formaldehyde, large parts of the atmospheric glyoxal (47%) and methylglyoxal (79%) are thought to be formed during the oxidation of isoprene emitted by vegetation (Fu et al., 2008, Wennberg et al., 2018).”

Line 57: Rather than citing “GEOS-Chem model simulations” for the lifetime, I would cite the papers that get that figure, such as Fu 2008

AC: The text has been rephrased accordingly (line 60).

Line 93: No comma needed after “They concluded”

AC: The comma has been erased (line 99).

Line 97: If the authors want to mention the A-train, include a brief

description of what that is. Otherwise, it does not seem necessary to include that information.

AC: In lines 102-103, the sentence has been changed to:

“More recently, (Stavrakou et al., 2016) examined emissions of crop residue fires in the North China Plain using data from the OMI satellite.”

Line 112: German should be capitalized

AC: German has been capitalized (line 118).

Table 1: “Temperature” is misspelled

AC: The typo has been corrected accordingly.

Line 172 or later: It’s not clear how the [C2H2O2] and [C3H4O2*] concentrations are derived from the mini-DOAS remote sensing measurement. Are they derived from the ODlimb line-of-sight measurement? Do we interpret that as the instantaneous concentration at the altitude of the aircraft? Particularly later, when the total column measurements are compared to the satellite measurements, it would be helpful to have that distinction made.

AC: Yes, we use the line-of-sight limb measurement of target and scaling gas to derive mixing ratios of the target gas for the altitude range of the aircraft, from where most of the absorption comes from. This is quantified by the so-called α -factors, which give the fraction of the absorption in altitude layer z_i relative to the total atmospheric absorption. They are derived from our DOAS measurement (SCD_X) and radiative transfer modelling of the respective Box air mass factors (B_{X_i}):

$$\alpha_j = \frac{\left(SCD_X - \sum_{i \neq j} [X]_i B_{X_i} z_i \right)}{SCD_X} \quad (1)$$

To clarify this aspect, lines 159-161 have been rephrased to:

“From the mini-DOAS limb measurements of the total slant column density, the concentration $[X]_j$ of the trace gas X in the atmospheric layer j (i.e., the altitude of the aircraft) is then determined from...”

Additionally, we have added in lines 167-169:

“When needed, the total atmospheric column density of the respective gases is approximated by integrating the measured lower and higher quartile profiles in incremental steps of 100m each (fig. 9).”

Line 175-181: Use the terms ODlimb and ODms instead of b and c for more clarity.

AC: The text has been rephrased accordingly (lines 190-193).

Figures 2 and 3: The various shapes of blue are hard to differentiate, and the markers are too small to really see the shapes.

AC: The colors of the curves in fig. 2 and 3 have been changed accordingly.

Figure 5: What time are the MODIS satellite images from? Beginnings of the flight? The panels numbers a-d are missing

AC: Panel numbers have been added within the figure panels. The time of each MODIS satellite image has been added to the figure caption:

“The MODIS satellite images are from 14:10 UTC (Sept. 11, 2014), 14:30 UTC (Sept. 16, 2014), 14:20 UTC (Sept. 18, 2014), and 17:55 UTC (Sept. 19, 2014).

The images were taken from NASA WORLDVIEW <https://worldview.earthdata.nasa.gov/>.”

Figure 9: It is very difficult to see the “C-shape” curve in the CO data that the authors discuss. Consider putting the x-axis on a log scale.

AC: The axis scaling has been changed accordingly and we have added in the figure caption:

“Note the logarithmic scale of the x-axis in panel a.”

Line 376: To remain consistent with the rest of the paper, use ppb instead of nmol/mol

AC: The text has been rephrased accordingly (line 401).

Line 357: “leading to their generally correlated vertical profiles”. Later on, the authors state that the formaldehyde vertical profile is markedly different from the other two. Clarify this?

AC: For clarification, line 376-378 has been changed to:

“As their dominant source, isoprene globally accounts for 67%, 47%, and 79% of the annual sources of formaldehyde, glyoxal, and methylglyoxal (Fu et al., 2008), respectively, leading to their rapidly decreasing vertical profiles.”

Figure 11: In the x-axis label, put which satellite(s) were used in each of the other papers.

AC: The figure has been changed accordingly.

Line 420: Are the emission ratios from the column integrated value or the concentration value?

AC: The emission ratios are derived from the inferred mixing ratios. For clarification, line 447 has been changed to:

“Instead, we use the inferred mixing ratios. . .”

Line 440: “Emissions of monoterpenes, like alpha-pinene, on the other hand, are at least one order of magnitude smaller”. This statement is unclear. Smaller than what?

AC: This compares the emissions of monoterpenes to those of isoprene (which dominate). Accordingly, line 470 has been changed to:

“Apparently, emissions of monoterpenes, like alpha-pinene, are at least one order of magnitude smaller than isoprene emissions.”

Reviewer Comment RC3:

Comments:

Lines 172-182: The writing in this paragraph is somewhat confusing. The statement of UV/vis limb measurements dividing the atmosphere in to three parts (a, b, and c) applies not only to O₄ absorption but also to the absorption of the targeted species. But here the authors only discussed the implication for O₄ absorption (i.e., b-c dominates, which is also true for the targeted species here). What are the implications for the retrievals of the targeted species?

AC: In order to clarify this, we added in lines 186-187 and 195-196:

“In the following, we discuss the significance of the different contributions exemplarily for O₄. Evidently, the same tri-partitioning applies for all other gases of interest, however differently weighted as expressed by the respective alpha-factors.”

“Figure 2 illustrates the contributions to OD_{meas} at 343.7 nm (panel 1a) and 477.3 nm (panel 2a) for O₄ as a function of the flight time for Sept. 16, 2014.”

Lines 194-197: “From the above discussion, ... volume.”: Can the authors say something about the estimated size and orientation of this averaging volume?

AC: Lines 208-212 have been changed to:

“From the above discussion, it also becomes clear that our air-borne UV/vis limb measurements average over some atmospheric volume, which is determined by the viewing angle of the telescope lenses (0.3°), the light path length, and the aircraft displacement during the time of measurement, both of which are in the order of several kilometers (for details see sect. 3, and fig. 6). This large sampling volume precludes direct comparisons with in situ measured quantities on spatial scales smaller than the current averaging volume.”

Other minor comments:

Line 13: “applaying” should be “applying”

AC: The typo has been corrected accordingly (line 14).

Line 31: Extra “is” after C₃H₄O₂*. Please remove.

AC: The extra ‘is’ has been erased (line 32).

Line 52-69: Missing key reference for the global budget of glyoxal: Myriokefalitakis et al. (2008) Myriokefalitakis, F., M. Vrekoussis, K. Tsigaridis, F. Wittrock, A. Richter, C. Brühl, R. Volkamer, J.P. Burrows, and M. Kanakidou, 2008: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution.

Atmos. Chem. Phys.,8,4965-4981, doi:10.5194/acp-8-4965-2008.

AC: The missing reference has been added in line 65-66:

“Satellite observations have shown strongly enhanced vertical column densities of atmospheric glyoxal above this region (e.g., Myriokefalitakis et al., 2008).”

Lines 85-87: “In comparison to satellite... biogenic precursors.” This statement is missing references.

AC: The sentence has been changed in lines 90-93 to:

“In comparison to satellite measurements from SCIAMACHY and GOME-2, several studies have found evidence that the models underestimate global glyoxal emissions, when not considering additional biogenic sources (Myriokefalitakis et al., 2008, Stavrakou et al., 2009b, Lerot et al., 2010).” Accordingly, the following references have been added:

Myriokefalitakis, S., et al. “The influence of natural and anthropogenic secondary sources on the glyoxal global distribution.” (2008).

Stavrakou, T., et al. “The continental source of glyoxal estimated by the synergistic use of spaceborne measurements and inverse modelling.” (2009).

Lerot, C., et al. “Glyoxal vertical columns from GOME-2 backscattered light measurements and comparisons with a global model.” *Atmos. Chem. Phys.* 10.24 (2010): 12-059.

Line 241: Remove “either of”

AC: The text has been rephrased accordingly (line 258).

Line 250: “several 100m” should be “several hundred meters”

AC: The text has been rephrased accordingly (line 267).

Figure 8 caption: “The colour coding in panels (e)), and (g)” should be “(e) and (f)”

AC: The sentence and the color coding have been removed.

Line 368: Extra “)” after (Fu et al., 2008). Also, there was no budget analysis for formaldehyde in Fu et al. (2008). Please cite a relevant reverence.

AC: The additional “)” refers to line 389-393: “(mostly... Fu (2008)).” The sentence has been changed to:

“Besides their common dominant precursor, additional sources of the gases differently influence their local distribution (mostly combustion processes and oxidation of other biogenic/anthropogenic hydrocarbons in the case of formaldehyde (Lee et al., 1998, Liu et al., 2007, Fortems et al., 2012), oxidation of acetylene in the case of glyoxal, and oxidation of acetone in the case of methylglyoxal (Fu et al., 2008)), and might therefore differently contribute to our measurements. A recent study additionally discussed the oxidation of aromatics as possible relevant source of atmospheric glyoxal and methylglyoxal (Taraborrelli

et al., 2020).”

These additional references for the budget analysis of formaldehyde are now included:

Lee, Y-N., et al. "Atmospheric chemistry and distribution of formaldehyde and several multioxygenated carbonyl compounds during the 1995 Nashville/Middle Tennessee Ozone Study." *Journal of Geophysical Research: Atmospheres* 103.D17 (1998): 22449-22462.

Fortems-Cheiney, A., et al. "The formaldehyde budget as seen by a global-scale multi-constraint and multi-species inversion system." *Atmospheric Chemistry & Physics Discussions* 12.3 (2012).

Liu, L., et al. "Photochemical modelling in the Po basin with focus on formaldehyde and ozone." (2007).

Line 733: Capitalize "C" in Nature "communications".

AC: Communications has been capitalized (line 768).

Additional changes in the manuscript by the authors:

- Title, line 10, line 517, table 3 (caption), line 575, line 589:** normalised → normalized
- Line 12:** "...chemical transport models..." has been added
- Line 44:** catalysed → catalyzed
- Line 57:** "...isoprene..." has been added.
- Line 67:** anthropogenicly → anthropogenically
- Line 69:** New reference added: (Taraborelli et al., 2020)
- Lines 91-92:** The sentence has been changed to: "...evidence that the models underestimate global glyoxal emissions, when not considering additional biogenic sources..."
- Lines 121-122:** The sentence has been changed to: "...and combined with previously reported emission factors of..."
- Line 126:** "present" has been removed
- Line 132, 232, 454, 485:** analysed → analyzed
- Figure 1 (caption, line 4):** fit → fitted
- Line 177:** A comma has been added: "...simulated, and..."
- Figure 2 (caption):** The sentence has been changed to: "The average line-of-sight photon path length...is plotted in panels 1b, 2b."
- Figure 2 (caption, line 1,4,5,6), Figure 3 (caption, line 1), Figure 8 (caption, line 1,2), Figure 9 (caption, line 1,3), lines 195, 298, 304, 308, 319, 327, 329, 358, 371, 408, 454, 495, 508:** Parentheses removed
- Figure 2, caption:** colour → color
- Line 203:** The sentence has been changed to: "...maximum values around 100 km."
- Lines 225,226:** Spacing corrected
- Line 232:** on the order → in the order
- Line 240, Figure 6 (caption), line 467:** centre → center
- Figure 6 (caption) and Figure 12 (caption):** colour coded → color-coded
- Line 289:** Environmenral → Environmental
- Line 310:** "...passed directly." → "...directly passed."
- Line 328:** "...photochemical and..." has been added.
- Figure 9 (caption):** "The black line shows..." → "The black lines show..."
- Figure 10 (caption):** "...(black)." → "...(grey)."
- Line 344-345:** To the sentence has been added: "...or to direct formation from longer-lived VOCs (e.g. phenols) (Andreae et al., 2001; Taraborrelli et al., 2020)."
- Line 381:** lead → contribute significantly
- Line 394:** anthropogenic emitted trace → anthropogenically emitted trace gas
- Line 400:** The sentence has been changed to: "...typical for air above..."
- Line 403:** To the sentence has been added: "...or a result of longer-lived oxidized aromatics (Taraborrelli et al., 2020)."
- Line 408:** The sentence has been changed to: "...contribution of the different precursor gases, their sinks due to photolysis and reaction with..."

Figure 11 (caption), line 422: column amounts → column densities
Line 424, 438: "panel" has been added
Line 456: Spacing corrected
Line 463: "of approximately 0.35" has been removed (repetition of line 456)
Line 512: previously described → described above
Line 515: "still missing" has been replaced by "not yet available"
Line 518: were → was
Line 541, 543, 545, 564: rounding corrected to two decimals instead of three
Line 559: airborne → air-borne
Line 578: seen → monitored
Line 621: To the sentence has been added: "...oxidation of methane and to a lesser degree of VOCs."
Lines 633-638: The following sentences have been added: "Taraborrelli et al., (2020) report in a recent study on long-lived VOCs like aromatics as a potential additional source of glyoxal in the free troposphere on a regional scale. Recent findings by Alvarado et al., (2020) reveal long range transport of glyoxal and formaldehyde within biomass burning plumes reaching distances of 1500 km downwind and thus enlarging the assumed local influence of biomass burning events on the tropospheric distribution of both gases. The time needed to reach such distances is in the order of several days, which implies the formation of glyoxal and formaldehyde from longer-lived precursors within the plumes."
Line 645: "aromatics" has been added
Line 647: behaviour → behavior

Profiling of formaldehyde, glyoxal, methylglyoxal, and CO over the Amazon: ~~Normalised~~ Normalized excess mixing ratios and related emission factors in biomass burning plumes

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Abstract. We report on airborne measurements of tropospheric mixing ratios and vertical profiles of formaldehyde (CH_2O), glyoxal ($\text{C}_2\text{H}_2\text{O}_2$, ~~and~~), methylglyoxal and higher carbonyls ($\text{C}_3\text{H}_4\text{O}_2^*$) (see below), and carbon monoxide (CO) over the Amazon Basin during the ACRIDICON-CHUVA campaign from the German High Altitude and Long-range research aircraft (HALO) in fall 2014. The joint observation of in situ CO and remotely measured CH_2O , $\text{C}_2\text{H}_2\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_2^*$, together with visible imagery and air mass back trajectory modelling using NOAA HYSPLIT (National Oceanic Atmospheric Administration, HYbrid Single-Particle Lagrangian Integrated Trajectory) allow us to discriminate between the probing of background tropical air, in which the concentration of the measured species results from the oxidation of biogenically emitted VOCs (mostly isoprene), and measurements of moderately to strongly polluted air masses affected by biomass burning emissions or the city plume of Manaus. For twelve near surface measurements of fresh biomass burning plumes, ~~normalised~~ normalized excess mixing ratios of $\text{C}_2\text{H}_2\text{O}_2$ and $\text{C}_3\text{H}_4\text{O}_2^*$ with respect to CH_2O are inferred and compared to recent studies. The mean glyoxal to formaldehyde ratio $R_{\text{GF}}=0.07$ (range 0.02–0.11) is in good agreement with recent reports which suggest R_{GF} to be significantly lower than previously assumed in global ~~CTM-models~~ chemical transport models (CTMs). The mean methylglyoxal to formaldehyde ratio $R_{\text{MF}}=0.98$ (range 0.09–1.50) varies significantly during the different observational settings, but overall appears to be much larger (up to a factor of 5) than previous reports suggest even when ~~applying~~ applying a correction factor of 2.0 ± 0.5 to account for the additional dicarbonyls included in the $\text{C}_3\text{H}_4\text{O}_2^*$ measurements. Using recently reported emission factors of CH_2O for tropical forests, our observations suggest emission factors of $\text{EF}_{\text{G}}=0.25$ (range 0.11 to 0.52) g kg^{-1} for $\text{C}_2\text{H}_2\text{O}_2$, and $\text{EF}_{\text{M}} = 4.7$ (range 0.5 to 8.64) g kg^{-1} for $\text{C}_3\text{H}_4\text{O}_2^*$. While EF_{G} agrees well with recent reports, EF_{M} is (like R_{MF}) slightly larger than reported in other studies, presumably due to the different plume ages or fuels studied. Our observations of these critical carbonyls and intermediate oxidation products may support future photochemical modelling of air pollution over tropical vegetation, as well as validate past and present space-borne observations of the respective species.

1 Introduction

Emissions from biomass burning are a large source of reactive gases and particulate matter to the atmosphere on a local, regional and up to the global scale (Crutzen and Andreae, 1990; Andreae and Merlet, 2001a; Andreae et al., 2001; Andreae and Merlet, 2001b). Pyrogenic emissions form a complex mixture of species that can change over the duration of the fire and undergo further chemical reactions as emissions are transported downwind. In consequence, biomass burning may have adverse effects on the atmospheric photochemistry, secondary aerosol formation and composition, and hence cloud formation and radiation, as well as human health. Therefore, accurate measurements of pyrogenic emissions, the evolution of fire plume composition and the formation and aging of aerosols are needed, but respective data are lacking for many species (e.g., Andreae and Merlet (2001a); Akagi et al. (2011); Stockwell et al. (2015); Andreae and Merlet (2001b)).

Among the manifold of species emitted in large amounts by fires or formed in their plumes are carbonyl compounds such as formaldehyde (CH_2O), glyoxal ($\text{C}_2\text{H}_2\text{O}_2$), methylglyoxal ($\text{C}_3\text{H}_4\text{O}_2$), 2,3-butanedione ($\text{C}_3\text{H}_6\text{O}_2$), and many others (e.g., Andreae and Merlet (2001b)). Here and further on, $\text{C}_3\text{H}_4\text{O}_2^*$ ~~is~~ denotes $\text{C}_3\text{H}_4\text{O}_2$ and other substituted dicarbonyls (cf. 2,3-butanedione) with visible absorption spectra similar to $\text{C}_3\text{H}_4\text{O}_2$, since they cannot be distinguished with the spectral resolution available in our limb measurements (sect. 2.1).

It is well known that in the atmosphere most of CH_2O is formed as an intermediate oxidation species from the degradation of CH_4 and from a suite of non-methane hydrocarbons (NMHCs) (Seinfeld and Pandis, 2013). CH_2O can further be directly emitted into the troposphere by biomass burning (e.g., Finlayson-Pitts and Pitts (2000); Andreae and Merlet (2001a); Wagner et al. (2002); Akagi et al. (2011); Seinfeld and Pandis (2013); Stockwell et al. (2015)), and from incomplete combustion as well as the direct emission by vegetation (Carlier et al. (1986) and references therein). Due to its short lifetime in the atmosphere of only several hours, CH_2O mixing ratios range from several 10 ppt to a few 100 ppt in the pristine (e.g., marine) environment. In the lower or polluted troposphere, mixing ratios might reach several ppb (e.g., Finlayson-Pitts and Pitts (2000); Jaeglé et al. (1997); Wagner et al. (2002); Borbon et al. (2012); Seinfeld and Pandis (2013) and others). Secondary formed CH_2O (for example from acetone photolysis) is an important source of HO_x radicals, in particular in the middle and upper troposphere (Jaeglé et al., 1997). Further, since CH_2O is considerably water soluble, it may participate in either acid or base ~~catalysed~~ catalyzed aldol-condensation reactions in the aerosol phase, hence contributing to secondary organic aerosol (SOA) formation (Wang et al., 2010). Numerous studies of formaldehyde emissions from biomass burning both in the laboratory and the field were undertaken in the past, and its emission factor appears to be fairly well established for the various studied fuel and fire types (e.g., Finlayson-Pitts and Pitts (2000); Andreae and Merlet (2001a); Wagner et al. (2002); Akagi et al. (2011); Seinfeld and Pandis (2013); Stockwell et al. (2015); Andreae and Merlet (2001b)). Based on this knowledge, models have generally been able to reproduce reasonably well the formaldehyde column densities observed by satellites (e.g., Dufour et al. (2009); Stavrakou et al. (2009b); Boeke et al. (2011); Bauwens et al. (2016), and others), or concentrations directly measured in the atmosphere (e.g., Arlander et al. (1995); Fried et al. (2008); Borbon et al. (2012); Kaiser et al. (2015); Chan Miller et al. (2017) and others).

Similar to formaldehyde, ~~glyoxal and methylglyoxal are formed by large parts of the atmospheric glyoxal (47 % and)~~
55 ~~and methylglyoxal (79 %, respectively,)~~ are thought to be formed during the oxidation of isoprene emitted by vegetation
~~(Fu et al. (2008); Wennberg et al. (2018))~~ (Fu et al., 2008; Wennberg et al., 2018). Recent air-borne and satellite measurements
identified the Amazon to be the world most prominent isoprene source region, with isoprene mixing ratios exceeding 6 ppb
~~isoprene~~ in the boundary layer by end of the dry season in September 2014 (Gu et al., 2017; Fu et al., 2019). These elevated
60 mixing ratios are a consequence of the large isoprene emission from the rain forest combined with a significantly prolonged
atmospheric lifetime of up to 36 hours (~~GEOS-Chem model simulations~~) (Fu et al., 2008) over the Amazon Basin compared to
the global mean of less than 4 hours (Fu et al. (2019), fig. 6a). Fu et al. (2019) suspected strong isoprene emissions combined
with low NO_x concentrations to lead to significantly suppressed OH-levels as a possible reason for the observed slower isoprene
oxidation in this regime. The longer isoprene lifetime and efficient vertical transport over the Amazon lead to elevated isoprene
75 mixing ratios not only within the boundary layer but also in higher altitudes (Fu et al. (2019), fig. 4d), where it is a possible
source for in situ glyoxal and methylglyoxal production in the free troposphere. Satellite observations have shown strongly
enhanced vertical column densities of atmospheric glyoxal above this region (e.g., Myriokefalitakis et al. (2008a)).

The second most important precursors of the trace gases are acetylene (mostly ~~anthropogeniely~~ anthropogenically emitted) for glyoxal and acetone (mostly biogenic) for methylglyoxal, but both gases are also formed during the oxidation of other
volatile organic compounds (VOCs), particularly alkenes, aromatics, and monoterpenes (~~Fu et al., 2008~~) (Fu et al., 2008; Taraborrelli et al.,
70 . For both gases, Fu et al. (2008) estimated their global source strengths to 45 Tg a⁻¹ and 140 Tg a⁻¹, respectively. Atmospheric lifetimes of glyoxal and methylglyoxal are only about 2 h, mostly due to photolysis and to a lesser degree due to
reactions with OH radicals (Koch and Moortgat, 1998; Volkamer et al., 2005a; Tadić et al., 2006; Fu et al., 2008; Wennberg
et al., 2018). Accordingly, in ambient air C₂H₂O₂ and C₃H₄O₂ mixing ratios typically do not exceed several 100 ppt (Fu
et al., 2008).

75 Glyoxal and methylglyoxal are additionally emitted in considerable quantities by biomass burning, their individual emission
strengths however are not yet well established (e.g., Andreae and Merlet (2001a); Akagi et al. (2011); Stockwell et al. (2015);
Zarzana et al. (2017, 2018); Andreae and Merlet (2001b)). The recent compilation of emission factors by Andreae and Merlet
(2001b) indicates for most reported fuels the complete lack of emission data for both dicarbonyls. Until the recent laboratory
and field studies by Zarzana et al. (2017, 2018), previous information on the glyoxal and methylglyoxal emissions from biomass
80 burning were based on only two laboratory studies (McDonald et al., 2000a; Hays et al., 2002). While (~~Hays et al., 2002~~)
Hays et al. (2002) reported larger emission factors for glyoxal compared to methylglyoxal, the recent findings of Zarzana et al.
(2017, 2018) indicated significantly smaller glyoxal emissions but larger emissions of methylglyoxal and other substituted
dicarbonyls in fires of agricultural biomass than those previously assumed in models (Fu et al., 2008).

Satellite and aircraft measurements of formaldehyde and glyoxal complemented by modelling have been used to study their
85 different atmospheric sources (e.g., Stavrou et al. (2009b); Boeke et al. (2011); Lerot et al. (2010); Chan Miller et al. (2014);
Bauwens et al. (2016); Stavrou et al. (2016), and others), the secondary aerosol formation from carbonyls (typically in the
background atmosphere), as well as in biomass burning plumes (Knote et al., 2014; Li et al., 2016; Lim et al., 2019), and even
more recently to estimate the organic aerosol abundance (Liao et al., 2019). Unlike for formaldehyde, the models had varying

success in reproducing the glyoxal column densities (~~Myriokefalitakis et al., 2008b; Stavrakou et al., 2009b; Lerot et al., 2010~~)
90 (Myriokefalitakis et al., 2008b; Stavrakou et al., 2009a; Lerot et al., 2010). In comparison to satellite measurements from SCIA-
MACHY and GOME-2, several studies have found evidence that the models underestimate global glyoxal emissions, when not
considering additional ~~secondary sources apart from those inferred from the oxidation of biogenic precursors~~biogenic sources
(Myriokefalitakis et al., 2008a; Stavrakou et al., 2009a; Lerot et al., 2010).

The ratios of $C_2H_2O_2$ to CH_2O (R_{GF}), and $C_3H_4O_2$ to CH_2O (R_{MF}) can be used as indications of the precursor VOC
95 species and to identify biomass burning in contrast to biogenic sources (Kaiser et al., 2015). In the past, R_{GF} has been studied
based on multiple ground-based observations as well as satellite measurements (e.g., McDonald et al. (2000a); Kaiser et al.
(2015); Chan Miller et al. (2017)). Kaiser et al. (2015) studied inferred R_{GF} over the south-eastern United States during
the 2013 SENEX (Southeast Nexus) campaign, and compared these measurements to respective OMI (Ozone Monitoring
Instrument) satellite retrievals. They concluded ~~;~~ that in regimes rich of monoterpene emissions R_{GF} is generally larger than
100 3 %, while regions dominated by isoprene oxidation appear characterized by low $R_{GF} < 3$ %. For a compilation of previously
inferred R_{GF} see Kaiser et al. (2015), Table 1.

More recently, Stavrakou et al. (2016) examined emissions of crop residue fires in the North China Plain using data from the
OMI satellite, ~~which is part of the so-called A-train (<https://atrain.nasa.gov/>).~~ Their inferred column emission ratio of 0.04–
0.05 was comparable to the R_{GF} observed by Zarzana et al. (2017), but smaller than those reported by McDonald et al. (2000a)
105 and Hays et al. (2002), which were used in the study of Fu et al. (2008). Nevertheless, the chemical transport model used by
Stavrakou et al. (2016) was able to reproduce the measured formaldehyde column densities and the glyoxal enhancements
observed over the North China Plain during the peak burning season.

Information on methylglyoxal in the atmosphere is even more rare, since to our knowledge satellite instruments measuring
methylglyoxal are not (yet) available, and atmospheric measurements of methylglyoxal are still sparse. This is a result of the
110 moderate spectral resolution of space- and air-borne optical measurements, which suffer from the spectral interference of the
major but only weakly structured absorption bands of methylglyoxal with those of other dicarbonyls (mainly 2,3-butanedione)
in the blue spectral region (Meller et al., 1991; Horowitz et al., 2001; Thalman et al., 2015; Zarzana et al., 2017). Potential
interferences with the 7ν absorption band of water vapour at 442 nm further complicate the spectral retrieval (Thalman et al.,
2015; Zarzana et al., 2017). In situ measurements of methylglyoxal using different techniques have only recently become
115 available (Thalman and Volkamer, 2010; Pang et al., 2011; Lawson et al., 2015; Michoud et al., 2018). The very limited number
of measurements in conjunction with insufficient detection limits are still preventing comprehensive studies of methylglyoxal.

Here we report on simultaneous measurements of CO , CH_2O , $C_2H_2O_2$, and $C_3H_4O_2^*$ in the lower to upper troposphere
over the Amazon Basin at the end of the dry season in 2014. All measurements were performed from the ~~german~~German
research aircraft HALO operated by the Deutsches Zentrum für Luft- und Raumfahrt (DLR). The simultaneous near surface
120 measurements of $C_2H_2O_2$ and $C_3H_4O_2^*$ allow us to estimate their emission ratios with respect to CH_2O as well as the normal-
ized excess mixing ratios within the probed biomass burning plumes, and ~~when~~ combined with previously reported emission
factors of CH_2O (e.g., Andreae and Merlet (2001b)), to estimate their emission factors for tropical forest fires. The joint mea-
surements of the carbonyls and CO in the middle and in the upper troposphere, more distant from their direct sources at the

ground, provides insight into their tropospheric profiles and precursors in a pristine atmosphere and under low NO_x conditions. Additionally, air mass backward trajectory modelling classifies the probed air masses and their possible origins.

The paper is organized as follows. Chapter 2 briefly describes the measurement techniques and methods used in the **present** study. Chapter 3 and 4 report on the ACRIDICON-CHUVA campaign and the actual measurements, and chapter 5 discusses the major findings and results. Chapter 6 concludes and summarises the study.

2 Methods

2.1 DOAS Measurements

The mini-DOAS instrument is a UV/vis/near-IR six channel optical spectrometer, which detects scattered skylight received from scanning limb and nadir directions. These spectra can be ~~analysed~~analyzed for absorption structures of O_4 , CH_2O , $\text{C}_2\text{H}_2\text{O}_2$ and $\text{C}_3\text{H}_4\text{O}_2^*$ (among other species). A video camera (type uEye UI-1005XS from IDS Imaging Development Systems GmbH) with a field of view of 46° is installed into the telescope unit and co-aligned with the spectrometer's limb telescopes. It provides visual imagery of the probed atmospheric scene at a rate of 1 Hz. An extensive description of the instrument and its deployment on the HALO aircraft can be found in Hüneke (2016); Hüneke et al. (2017). The mini-DOAS instrument remotely probes the atmosphere with the limb telescopes (FOV 0.5° vertical, 3.15° horizontal) oriented perpendicular and right hand to the aircraft main axis. Although the limb telescopes can be directed at any elevation angle for traditional atmospheric profiling, during the ACRIDICON-CHUVA campaign they were constantly directed at 0.3° below the horizon, for optimal measurements when using the O_4 scaling method (Hüneke (2016); Hüneke et al. (2017); Stutz et al. (2017); Werner et al. (2017), and below).

The post-flight analysis of the collected limb spectra includes a DOAS (Differential Optical Absorption Spectroscopy (Platt and Stutz, 2008)) analysis of the measured skylight spectra for the absorption structures of O_4 , CH_2O , $\text{C}_2\text{H}_2\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_2^*$ as well as the attribution of the measured absorption to the correct locations in the atmosphere. The latter is performed using the O_4 scaling method described in detail in Hüneke (2016); Hüneke et al. (2017); Stutz et al. (2017),2 as well as below. The DOAS analysis of the data is performed according to the settings in Tables 1 and 2.

Exemplary sample retrievals of CH_2O , $\text{C}_2\text{H}_2\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_2^*$ are shown in fig. 1. The detection of $\text{C}_3\text{H}_4\text{O}_2^*$ (fig. 1, panel (3) ~~)~~ deserves a brief discussion. It is known that substituted dicarbonyls such as biacetyl ($\text{CH}_3\text{COCOCH}_3$), with absorption cross sections in the visible spectral range similar to those of $\text{C}_3\text{H}_4\text{O}_2$, are also co-emitted from biomass fires in significant quantities (e.g., Meller et al. (1991); Horowitz et al. (2001); Thalman et al. (2015); Zarzana et al. (2017)). Owing to the moderate resolution of our spectrometer in the visible spectral range (full width half maximum resolution of 1.1 nm or 8.4 pixels, see Hüneke (2016)), we cannot separately (and thus unambiguously) detect these substituted dicarbonyls in the atmosphere, unlike in studies employing higher resolving spectrometers (e.g., Thalman et al. (2015)). Accordingly, we report here the weighted sum (absorption cross section times concentration) of $\text{C}_3\text{H}_4\text{O}_2$ and that of other substituted dicarbonyls and express that quantity as $\text{C}_3\text{H}_4\text{O}_2^*$.

Table 1. Trace gas absorption cross sections used for the DOAS based spectral retrieval.

No.	Absorber	Temperatur <u>Temperature</u> [K]	Reference	Uncertainty [%]
1	O ₄	273	Thalman and Volkamer (2013)	4
2	O ₃	203	Serdyuchenko et al. (2014)	3
3	O ₃	273	Serdyuchenko et al. (2014)	3
4	NO ₂	273	Burrows et al. (1998)	4
5	H ₂ O	293	Rothman et al. (2009)	
6	CH ₂ O	293	Chance and Orphal (2011)	10
7	C ₂ H ₂ O ₂	296	Volkamer et al. (2005b)	3
8	C ₃ H ₄ O ₂	296	Meller et al. (1991)	10
9	C ₄ H ₆ O ₂	223	Horowitz et al. (2001)	4

Table 2. Details of the DOAS spectral analysis for the various trace gases.

Target gas	Spectral interval [nm]	Fitted absorbers (see Table 1)	Add. Param.	Polyn.	σ [dSCD]
O ₄	348–369	1, 2, 3, 4, 6	I _{Ofs} ⁽ⁱ⁾ , R ⁽ⁱⁱ⁾ , R · $\lambda^{4(iii)}$	2	8×10^{41}
	460–490	1, 2, 3, 4, 5	I _{Ofs} , R, R · λ^4	2	4×10^{41}
CH ₂ O	324–354	1, 2, 3, 4, 6	I _{Ofs} , R, R · λ^4	2	5×10^{15}
C ₂ H ₂ O ₂	420–439 and 447–465	1, 3, 4, 5, 7	I _{Ofs} , R, R · λ^4	2	1×10^{15}
C ₃ H ₄ O ₂ *	420–475	1, 3, 4, 5, 7, 8, 9	I _{Ofs} , R, R · λ^4	2	1×10^{16}

(i) I_{Ofs}: Offset spectrum; (ii) R: Ring spectrum; (iii) R · λ^4 : Ring spectrum multiplied by λ^4 .

From the retrieved slant column densities, absolute concentrations of the targeted gases are inferred using the recently developed O₄ scaling method. As shown in previous studies, the scaling method is based on simultaneous measurements of the target gas X and a scaling gas P of known concentration (here the collision complex O₂–O₂, briefly called O₄) in the same wavelength interval (Hüneke, 2016; Hüneke et al., 2017; Stutz et al., 2017; Werner et al., 2017). ~~The concentration~~ From the mini-DOAS limb measurements of the total slant column density, the concentration [X]_j of the trace gas X in the atmospheric layer j (i.e., the altitude of the aircraft) is then determined from

$$[X]_j = \frac{\alpha_{X_j}}{\alpha_{P_j}} \cdot \frac{SCD_X}{SCD_P} \cdot [P]_j \quad (1)$$

(see Stutz et al. (2017), eq. (14)). Here, [P]_j is the calculated extinction of O₄ ($\epsilon_{O_4} = \sigma \cdot k_{eq} \cdot [O_2]_j^2$) in the atmospheric layer j, from which we take the sample. SCD_P is the measured optical depth of O₄ and SCD_X is the measured slant column density of the target gas X. The α -factors α_{X_j} and α_{P_j} each express the ratio of the absorption of the gas in layer j to the total atmospheric absorption. Usually, the α -factors are simulated in supporting radiative transfer calculations using the Monte Carlo model McArtim (Deutschmann et al., 2011; Knecht, 2015). When needed, the total atmospheric column density of the respective

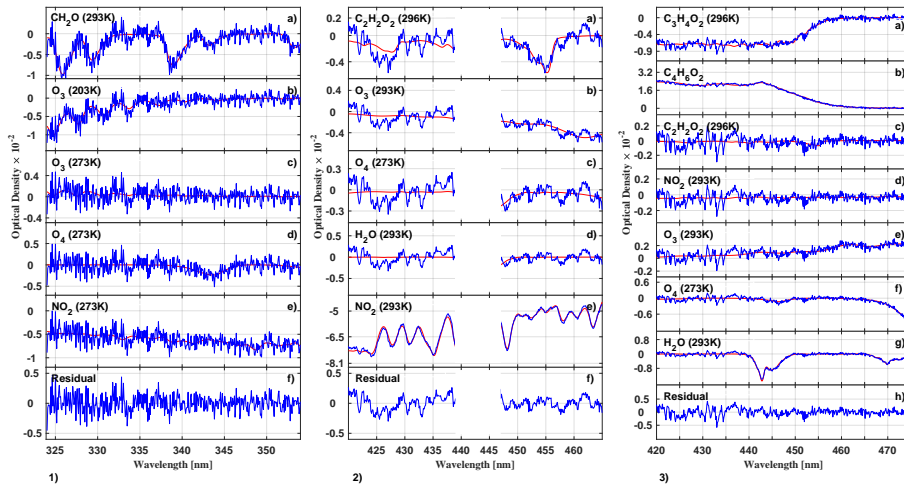


Figure 1. Inferred absorption spectra of CH_2O (1), $\text{C}_2\text{H}_2\text{O}_2$ (2), and $\text{C}_3\text{H}_4\text{O}_2^*$ (3) for the measurements at 17:16, 15:06 and 14:53 UTC, respectively, during the flight on Sept. 11, 2014 (AC11). The traces shown in blue are the inferred atmospheric spectra together with the residual spectral structures, the red line shows the reference spectra of the respective gases. In order to avoid cross correlations with the 7ν absorption band of H_2O at 442 nm, $\text{C}_2\text{H}_2\text{O}_2$ is simultaneously fit-fitted over two separated spectral windows, ranging from 420 nm to 439 nm and 447 nm to 465 nm.

gases is approximated by integrating the measured lower and higher quartile profiles in incremental steps of 100 m each (fig. 9).

170 When applying the scaling method to air-borne UV/vis spectroscopy in limb geometry, a powerful radiative transfer model is necessary to treat the radiative transfer in 2D or 3D, calculate the refraction and also account for the sphericity of the Earth. We use the Monte Carlo radiative transfer model McArtim (Deutschmann et al., 2011), where each measurement is modelled forward while considering the actual atmospheric, instrumental, and observational (e.g., Sun position relative to the pointing) parameters, the geolocation and the pointing of the telescope as described in Hüneke (2016); Hüneke et al. (2017). Further,
 175 a combination of climatological aerosol profiles obtained by LIVAS (Amiridis et al., 2015) and the Stratospheric Aerosol and Gas Experiment II (SAGE II) (https://eosweb.larc.nasa.gov/project/sage3/sage3_tablehttps://eosweb.larc.nasa.gov/project/sage3/sage3_table) is considered. For the calculation of the α -factors, box air mass factors are simulated and-summed-, and summed weighted by concentration (Stutz et al. (2017), eq. (11)). We calculate the extinction $[P]_j$ to obtain the vertical O_4 profile. For the target gases CH_2O , $\text{C}_2\text{H}_2\text{O}_2$, $\text{C}_3\text{H}_4\text{O}_2^*$, we assume exponentially decaying profiles. The latter appears justified
 180 because of photochemical arguments, the source distribution (mostly surface), the photochemical lifetimes, the time scales of possible vertical transport, as well as when inspecting the profile shapes obtained in the post-analysis (fig. 9).

Evidently, UV/vis limb measurements naturally divide the atmosphere into three different layers, which are separated by the different contributions to the total absorption or optical depth (OD). These contributions are (a) the overhead absorption (OD_{oh}), (b) the absorption located within the line-of-sight of the telescopes (OD_{limb}) (of which most, but not all is due to single
 185 scattering), and (c) the absorption below the line of sight (OD_{ms}) (of which the photon paths are necessarily all of higher scat-

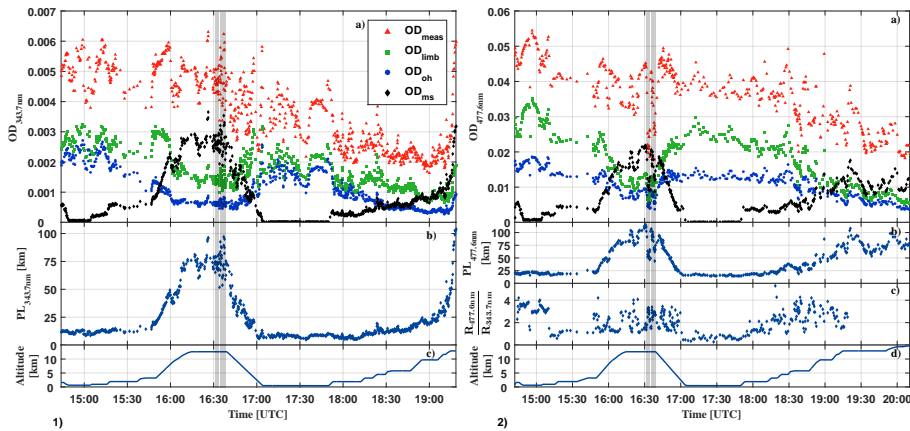


Figure 2. Attribution of the total measured optical depth of O_4 at 343.7 nm (panel (1)) on the left and at 477.6 nm (panel (2)) on the right) to the various fractions, i.e., absorption from overhead the aircraft (OD_{oh}), from multiple scattering below the aircraft (OD_{ms}), within the line-of-sight of the telescopes (OD_{limb}), and the total measured optical depth of O_4 (OD_{meas}) for the HALO flight on Sept. 16, 2014 (AC11) (panels (1a), (2a)). The average line-of-sight photon path length inferred from the measured OD_{meas} at 343.7 nm and 477.6 nm, respectively, as a function of the flight time (is plotted in panels (1b), (2b)). The colour ratio $\frac{R_{343.7}}{R_{477.6}}$ of the measured radiances at 343.7 nm versus 477.6 nm is shown in panel (2c). The flight trajectory of the HALO aircraft is shown in panels (1c) and (2d). The sharp drop of the optical depth between 16:32–16:34 UTC and 16:35–16:39 UTC (grey bars) coincides with the passage of a cumulonimbus cloud in front of the telescopes. For details see the text.

tering order). In the following, we discuss the significance of the different contributions exemplarily for O_4 . Evidently, the same tri-partitioning applies for all other gases of interest, however differently weighted as expressed by the respective alpha-factors. For a high-flying aircraft, OD_{oh} has the least uncertainty since O_4 absorption approximately scales with $[O_2]^2$ and the optical state of the overhead atmosphere is well known. Therefore, the remainder-remainder of the measured total O_4 absorption has to be due to the varying contributions of (b) and (c) OD_{limb} and OD_{ms} , which are mostly modulated by the current low level cloud cover and ground albedo (Stutz et al. (2017), fig. 7). The knowledge of the α -factor however gives a handle on the relative fractions (b) and (c) OD_{limb} and OD_{ms} , since contribution (b) OD_{limb} can be calculated from $OD_{limb} = \alpha \cdot OD_{meas}$, and accordingly $OD_{ms} = OD_{meas} - OD_{oh} - OD_{limb}$. Still, the calculated attributions of (b) and (c) OD_{limb} and OD_{ms} to OD_{meas} can only be approximated due to the assumptions made regarding the current aerosols distribution and the cloud coverage.

195 Figure 2 illustrates the contributions to OD_{meas} at (panel (343.7 nm (panel 1a)) and (panel (and 477.3 nm (panel 2a)) for O_4 as a function of the flight time for Sept. 16, 2014. Figure 3 shows the same data, but sorted by flight altitude to demonstrate the relative change of the contributions. For 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_4 absorption dominates with > 50 up to 10 altitude, with a relative minimum. A relative minimum can be seen at the top of the planetary boundary layer at approximately 2 km, where often stratocumulus clouds prevail over the Amazon. Further, a maximum of OD_{limb} is visible at about 4 km, most probably a result of the increasing horizontal visibility with altitude and the moderate contribution of reflected multiple scattered

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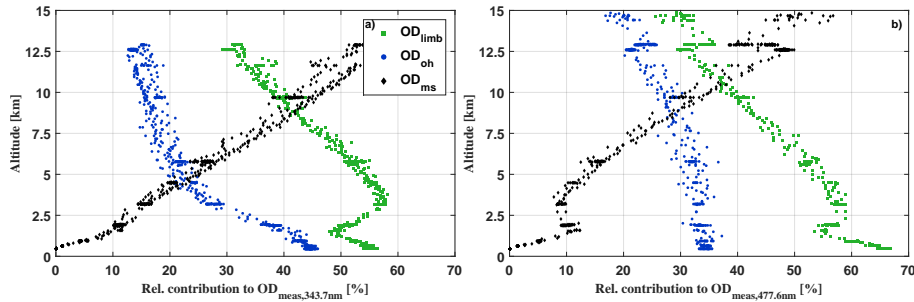


Figure 3. Relative contribution to the limb measured optical depth of O_4 at 343.7 nm (panel (a)) and at 477.6 nm (panel (b)) due to the absorption overhead the aircraft (OD_{oh}), from multiple scattering (OD_{ms}), and within the line of sight of the telescopes (OD_{limb}) for the HALO flight on Sept. 11, 2014 (AC11). For details see the text.

photons from the lower atmosphere to the total O_4 absorption. In the upper troposphere, the relative contribution of OD_{limb} to OD_{meas} decreases while the effective horizontal light paths become longer and reach maximum values of over 75 around 100 km. But given all uncertainties in the details of the actual atmospheric aerosol content, the cloud structure and coverage and their optical properties, it is more reasonable to speak here of an indication rather than a determination of the photon path lengths.

Fortunately, these uncertainties do not propagate into the uncertainty of the α -factor ratio and hence into the determination of $[X]_j$, provided the gases X and P have similar profile shapes (Knecht, 2015; Hüneke et al., 2017; Stutz et al., 2017). From the above discussion, it also becomes clear that our air-borne UV/vis limb measurements average over some atmospheric volume, which is determined by the viewing angle of the telescope lenses (0.3°), the light path length, and the aircraft displacement during the time of measurement, both of which are in the order of several kilometers (for details see sect. 3, and fig. 6). This large sampling volume precludes direct comparisons with in situ measured quantities on spatial scales smaller than the current averaging volume. This is of relevance to our study, for example when adding information from in situ measurements like CO to the analysis of our data.

Summing-up all described uncertainties, the precision error of the combined methods is can be approximately calculated according to eq. (1) as

$$[\Delta X]_j = \sqrt{\left(\frac{\Delta\alpha_{R,j}}{\alpha_{R,j}}\right)^2 + \left(\frac{\Delta S_{X,j}}{S_{X,j}}\right)^2 + \left(\frac{\Delta S_{P,j}}{S_{P,j}}\right)^2 + \left(\frac{\Delta P_j}{P_j}\right)^2} \cdot [X]_j, \quad (2)$$

where $\Delta\alpha_{R,j}$ accounts for (a) random Mie extinction, (b) small scale variability of the target and scaling gas mixing ratios at flight level and (c) uncertainty in the sampling contribution as discussed in fig. 2 and 3. The slant column errors $\Delta S_{X,j}$ and $\Delta S_{P,j}$ account for (a) uncertainty of the inferred fraunhofer reference SCD and (b) the DOAS Fit-fit error. ΔP_j accounts for the uncertainty of the in situ mixing ratio of the scaling gas, which in the case of O_4 scales with the air density and is accordingly limited by the measurement uncertainty of pressure and temperature. Additionally, the systematic errors of the individual absorption cross sections need to be added to $\Delta S_{X,j}$ according to Table 1. An extensive discussion of the total error

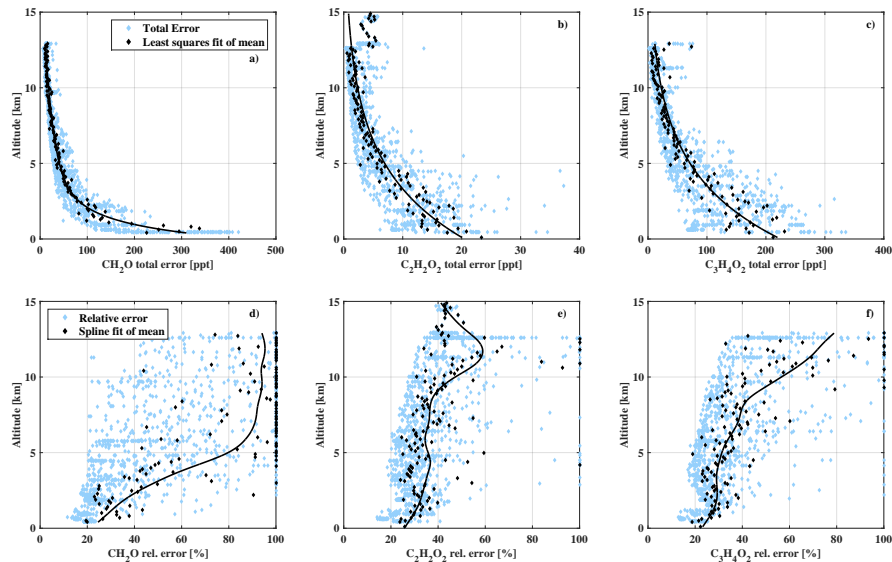


Figure 4. Relative and absolute total precision error of all measurements as a function of the measurement altitude.

budget of the O₄ scaling can be found in Hüneke (2016). While ΔP_j and $\Delta \alpha_{R,j}$ contribute approximately constantly to the
 225 total error budget, $\Delta S_{X,j}$ strongly increases with decreasing slant column density. For mixing ratios below 1 ppb (CH₂O),
 0.15 ppb (C₂H₂O₂), and 1.3 ppb (C₂H₄O₂*), the total precision error is strongly dominated by $\Delta S_{X,j}$. For higher mixing
 ratios, $\Delta \alpha_{R,j}$ and $\Delta S_{X,j}$ contribute in equal parts in the cases of C₂H₂O₂ and C₂H₄O₂*. For CH₂O, $\Delta \alpha_{R,j}$ is the major error
 factor for mixing ratios above 1 ppb, and $\Delta S_{X,j}$ only makes up 30 % of the total error. For all gases, ΔP_j never exceeds 7 % of
 the total precision error. Due to the strong dependence of $\Delta S_{X,j}$ on the slant column density and the exponentially decreasing
 230 vertical profiles of the gases, the resulting total precision errors $[\Delta X]_j$ are strongly altitude dependent (fig. 4). They range from
 16 % to 100 % for CH₂O, 17 % to 100 % for C₂H₂O₂, and 16 % to 100 % for C₂H₄O₂*. This study focuses on measurements
 below 2 km altitude, with mean total errors of the analysed-analyzed biomass burning events on-in the order of 21 % for CH₂O
 (upper and lower limit of the total precision errors are 350 ppt and 740 ppt), 25 % for C₂H₂O₂ (total errors from 30 ppt to
 45 ppt), and 22 % for C₂H₄O₂* (total errors from 240 ppt to 560 ppt).

235 2.2 AMTEX CO Measurements

In situ CO measurements were performed using an Aero-Laser 5002 vacuum UV resonance fluorescence instrument (Gerbig
 et al., 1996, 1999) installed in the cabin of the HALO aircraft. Main components of the CO instrument include a fluorescence
 chamber, resonance lamp, optical filter, two dielectric mirrors, and a pump. Atmospheric air is sampled through a backward-
 facing inlet mounted on top of the HALO fuselage. CO molecules in the ambient air are excited in the chamber by radiation
 240 from a radio frequency discharge resonance lamp. The wavelength range (centre-center line 151 nm with a bandwidth of 9 nm)
 is selected by the optical filter and the mirrors. The fluorescence signal is detected by a photomultiplier. The flow rate of the

sample air through the fluorescence chamber is set to 40 mL min^{-1} (STP). The sample air is dried with a SICAPENT trap (granulated phosphorus pentoxide drying agent) to eliminate a cross-sensitivity to water vapour.

245 The CO measurements are made at 1 Hz with a precision of 1.5 ppb. The accuracy is given by the precision and systematic errors caused by the drift of the background signal and sensitivity of the instrument, and the uncertainty of the CO calibration standard. The total accuracy amounts to $1.5 \text{ ppb} \pm 2.4\%$ (Gerbig et al., 1999). The CO instrument has been deployed during many aircraft campaigns using the DLR Falcon (e.g. Huntrieser et al. (2016a, b)) and was used for the first time used on board HALO during the ACRIDICON-CHUVA campaign (Wendisch et al., 2016).

3 Measurements

250 The ACRIDICON-CHUVA aircraft campaign took place from the operational basis Manaus (Brazil) within the period September and early October 2014 with a total of 14 scientific flights over the Amazon region. An overview of all ACRIDICON-CHUVA flight tracks can be found in Wendisch et al. (2016), fig. 6. The campaign aimed to improve the understanding of tropical deep convective clouds and their interaction with biogenic and anthropogenic aerosols, and also included precipitation formation and air pollution studies. A detailed description of the campaign objectives, the participating instruments and
255 research groups is given in Wendisch et al. (2016).

Our study requires simultaneous measurements of CH_2O , $\text{C}_2\text{H}_2\text{O}_2$, $\text{C}_3\text{H}_4\text{O}_2^*$ and O_4 (performed by the mini-DOAS spectrometers in the UV and visible spectral ranges as described in sect. 2.1) as well as CO measurements (performed by the AMTEX instrument, see sect. 2.2), but ~~either of~~ the instruments occasionally failed. Therefore, only for a subset of flights joint data is available. Further, since a part of the flights focused on objectives other than near surface air pollution, here we only
260 present data from four out of the 14 ACRIDICON-CHUVA flights, i.e. those of Sept. 11th (AC09), 16th (AC11), 18th (AC12), and 19th (AC13) in 2014. Nevertheless, the data collected during these flights provides valuable information on the different measured pollutants, their sources, atmospheric transformation and transport in pristine background air in the troposphere as well as fresh and aged air affected by biomass burning in the Amazon.

Each of these measurement ~~flight~~ flight flights took seven to eight hours, typically occurring between 14 UTC and 22 UTC, i.e.
265 during daytime. The long flight time supported the sampling of a large geographical area of the rain forest during the four flights, reaching from approximately 6° S to 8° N , and 49° W to 63° W . The detailed flight tracks and respective altitudes are shown in fig. 5. During each of these flights, the probed altitudes ranged from several ~~100~~ hundred meters up to 15 km, with flight sections inside the planetary boundary layer overpassing large agricultural areas (AC12 and AC13) as well as the rain forest and the Amazon river delta (AC09 and AC11, fig. 5).

270 Due to the relatively large, but patchy cloud cover over the Amazon, the UV and vis limb radiances varied significantly during the flights. Therefore, typical integration times of the measured co-added sets of skylight spectra range from seconds (under clear sky conditions) to several minutes (during cloudy sky and hazy conditions). In consequence, the along track resolution of the measurements was typically several kilometres in addition to the horizontal resolution perpendicular to the aircraft determined by radiative transfer (sect. 2.1). For the biomass burning events AC11-1 to AC11-3 (Table 3 and sect. 5.4),

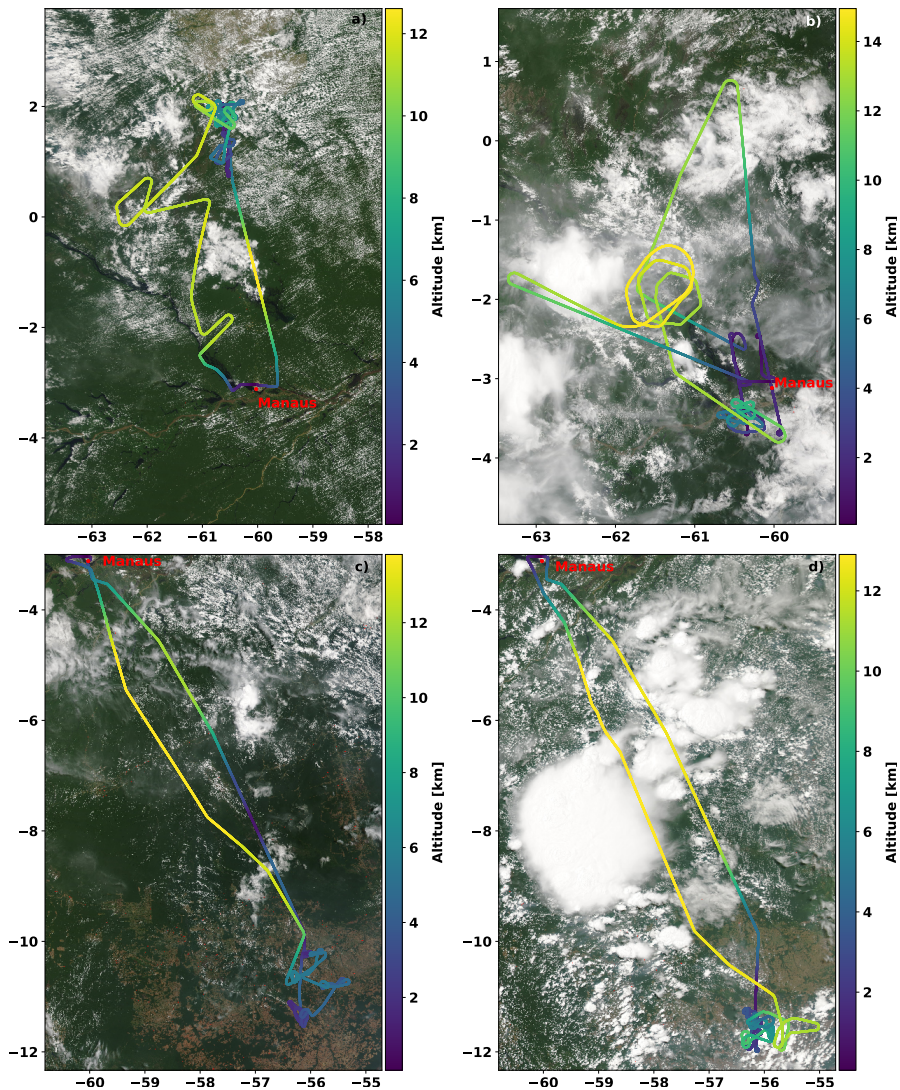


Figure 5. Tracks of the ACRIDICON-CHUVA flights (a) on Sept. 11, 2014, (b) on Sept. 16, 2014 (AC11), (c) on Sept. 18, 2014 (AC12), and (d) on Sept. 19, 2014 (AC13). All flights started and ended at the operational base Manaus airport in Brazil (red dot). The ~~colour~~ color coding indicates the flight altitude. The MODIS satellite images are ~~taken from NASA WORLDVIEW and are updated daily 14:10 UTC (Sept. 11, see https2014), 14://worldview30 UTC (Sept. earthdata16, 2014), 14:20 UTC (Sept. nasa18, 2014), and 17:55 UTC (Sept. gov/19, 2014).~~ The images were taken from NASA WORLDVIEW <https://worldview.earthdata.nasa.gov/>.

275 a two-dimensional visualization of the resulting averaging (or probed) areas per single measurement is indicated by the blue areas in fig. 6. The identification of the atmospheric measurement conditions and in particular of each biomass burning event is based on visual imagery using the recorded video data stream (fig. 7). In the following, only those measurements are claimed to be affected by biomass burning, for which the actual plumes are visible in the recorded images and are in the telescope's line of

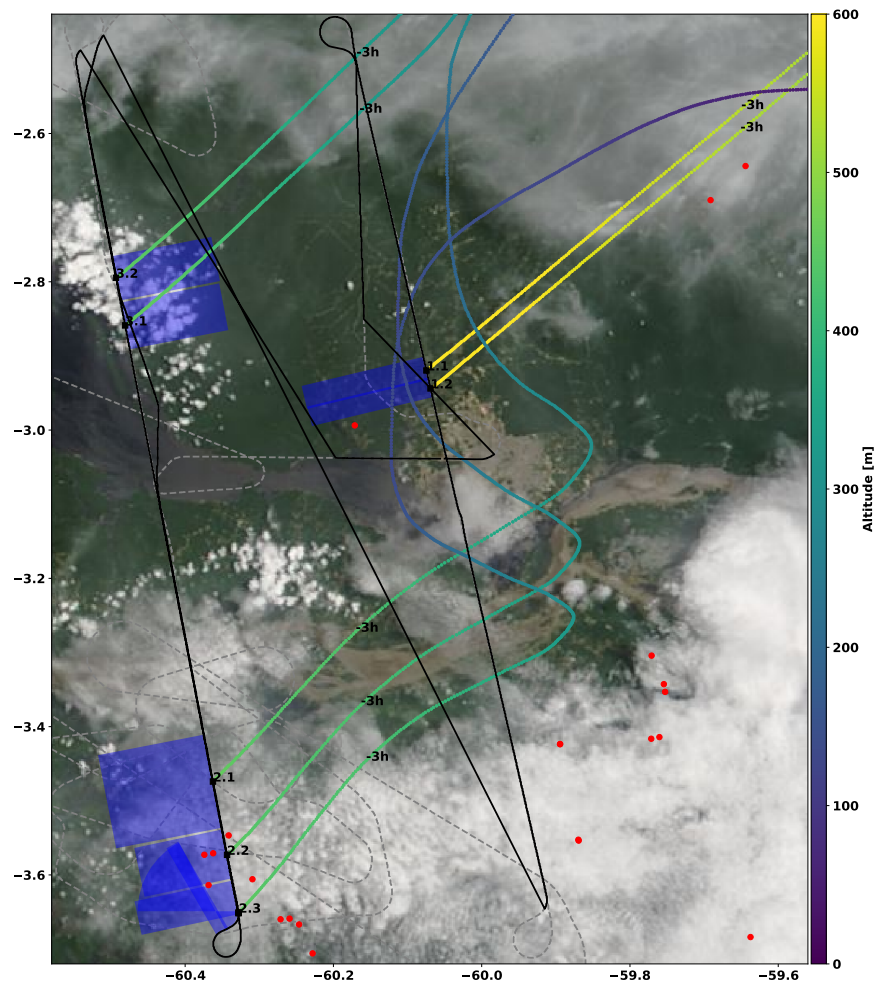


Figure 6. Zoom of the flight track for AC11 on Sept. 16, 2014. The flight tracks below/above 1000 m altitude are labelled by drawn/dashed lines, respectively. The take-off and landing of the aircraft was from Manaus airport (3.1° S, 60.0° W) located in the ~~centre~~center of the image. The biomass burning events detected by the MCD14 MODIS instrument on the Terra and Aqua satellites are indicated with red dots (not to scale). The biomass events probed by the mini-DOAS instrument are marked by black numbers next to the flight track, according to the labelling of Table 3. The blue rectangles approximately indicate the probed air masses in the horizontal plane, where the distance perpendicular to the flight track is given by the O_4 estimated photon path lengths (14 to 19 km), and the along track distance (3 to 15 km) by the spectrum integration time (33 to 166 s) multiplied by the aircraft ground speed (approximately 95 m s^{-1}) (sect. 2.1). For each biomass burning event, 3 h backward air mass trajectories were calculated and plotted ~~colour-coded~~color-coded by the altitude of the air mass. The MODIS satellite image was taken from NASA WORLDVIEW, see [https://worldview](https://worldview.earthdata.nasa.gov/)<https://worldview.earthdata.nasa.gov/>.

sight. These events are listed in Table 3. Depending on the flight pattern and the integration time of the spectra, some of these



Figure 7. Images taken by the mini-DOAS camera during events 1–6 (as indicated in fig. 6 and 8) for the flight AC11 with the UTC time given in each image. The second image was taken from the respective flight report. The video camera points into the same direction as the three limb telescopes of the mini-DOAS spectrometer, however with a much larger field of view of $\sim 46^\circ$ width.

280 plumes were intercepted more than once. In total, eight distinct plumes were probed during twelve individual measurements, all of which were recorded below 2 km flight altitude.

The MODIS instrument on board the Terra and Aqua satellites (MCD14, collection 6, available online from <https://worldview.earthdata.nasa.gov/>,

doi:10.5067/FIRMS/MODIS/MCD14DL.NRT.006) reports additional fires in the vicinity of the aircraft trajectory, which were

285 not directly located within ~~in~~ the field of view of the mini-DOAS telescopes, nor within the larger field of view of the camera.

Therefore, these events are not ~~more closely~~ further investigated in our analysis. However, the emissions of these fires are likely to have created an atmospheric background generally affected by differently aged biomass burning emissions within the boundary layer (fig. 6). Further insights into the recent photochemical past of the air masses are provided by 3 h backward air

mass trajectories calculated using the READY (Real-time ~~Environmental~~ Environmental Applications and Display sYstem)

290 website of the NOAA HYSPLIT model (<https://www.ready.noaa.gov/HYSPLIT.php>) (Stein et al., 2015; Rolph et al., 2017).

Exemplary 3 h backward trajectories are shown for events AC11-1.2 to AC11-3.2 in fig. 6. They indicate, that prior to detection all air masses resided well within the boundary layer, but did not directly pass over any additional reported fire.

However, all identified biomass burning events show large and correlated enhancements of CH_2O , $\text{C}_2\text{H}_2\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_2^*$, with mixing ratios up to 4.0 ppb, 0.26 ppb, and 2.8 ppb, respectively (fig. 8). Due to the differently sized spatial resolutions of

295 both instruments (sect. 2), the detected peaks in CO and those of CH₂O, C₂H₂O₂, and C₃H₄O₂^{*} do not (and are not expected to) strictly correlate. Therefore, we refrain from directly estimating emission ratios with respect to CO.

4 Results

Figure 8 shows the inferred volume mixing ratios of CH₂O (panel (a)a), C₂H₂O₂ (panel (b)b), C₃H₄O₂^{*} (panel (c)c), and CO (panel (d)d) for flight AC11 on Sept. 16, 2014. The measured trace gas mixing ratios are the largest for flight sections within the planetary boundary layer (14:45 to 15:15 UTC and 17:05 to 17:45 UTC), and the lowest in the upper troposphere (16:15 to 16:45 UTC and 19:15 to 20:20 UTC). Notable are the peaks in CO while flying through the Manaus city plume (grey bars) or biomass burning plumes (red bars). Elevated mixing ratios of CH₂O, C₂H₂O₂, and C₃H₄O₂^{*} can be related to biomass burning as well as to air masses of presumably aged background air (labelled with the green bars) as evidenced by the only moderately elevated CO. Here, the numbers (1) to (6) in panel (a)a of fig. 8 denote biomass burning affected air (1–3), air of the Manaus city plume (4), pristine air of the upper troposphere (5), and boundary layer air above the tropical forest (6). Sky images of all six different situations are shown in fig. 7.

4.1 Vertical profiles

Below 450 m altitude, CO mixing ratios range from 88.6 ppb to 291.8 ppb (fig. 9, panel (a)a), with a mean of [CO]=188.1 ppb. Within the planetary boundary layer, CO mixing ratios increase from 88.4 ppb to 2308 ppb (mean [CO] = 212.8 ppb), with peak mixing ratios above 500 ppb appearing when biomass burning plumes are ~~passed directly~~ directly passed. Lowest [CO] mixing ratios in the range of 55.1 ppb to 231.9 ppb (mean [CO] = 86.3 ppb) are found in the middle troposphere between 6 and 8 km altitude. In the upper troposphere (12–14 km), CO increases from 52.5 ppb to 212.6 ppb (mean [CO] = 134.5 ppb). In the convective tropics, C-shaped CO profiles are a well-known phenomenon, caused by the rapid transport of near surface CO rich air by meso-scale convective systems into the upper troposphere (e.g., Brocchi et al. (2018); Krysztofiak et al. (2018)).

315 When binning the data in 100 m altitude intervals and averaging over the lower and upper data quartiles within each interval, another maximum forms around the top of the boundary layer. Most likely, this suggests that over the Amazon biomass burning plumes often detrain their pollutants near the top of the boundary layer (cf. see for example the image at 17:24 UTC, fig. 7).

Inferred [CH₂O] ranges from 4.5 ppb near the surface to mean mixing ratios of 30 ppt in the upper troposphere (above 10 km). Mixing ratios within the boundary layer and middle troposphere vary significantly (fig. 9, panel (b)b). In part, this might be a manifestation of the direct emission of CH₂O into the lower part of the atmosphere, or the in situ formation of CH₂O during the oxidation of biogenic VOCs (BVOCs) as well as partly oxidized VOCs (OVOCs). Figure 10 puts our CH₂O measurements over the Amazon into the context of previously published CH₂O observations all over the world. Within this comparison, it is remarkable that the lowest CH₂O mixing ratios measured over the Amazon approximately agree with CH₂O measured within the boundary layer and middle troposphere over the West Pacific by Peters et al. (2012). Our measurements in the upper troposphere compare well to findings from Dufour et al. (2009) and Boeke et al. (2011) over Brazil and North America, respectively. The lowest mixing ratios measured in the middle and upper troposphere may reflect CH₂O formed

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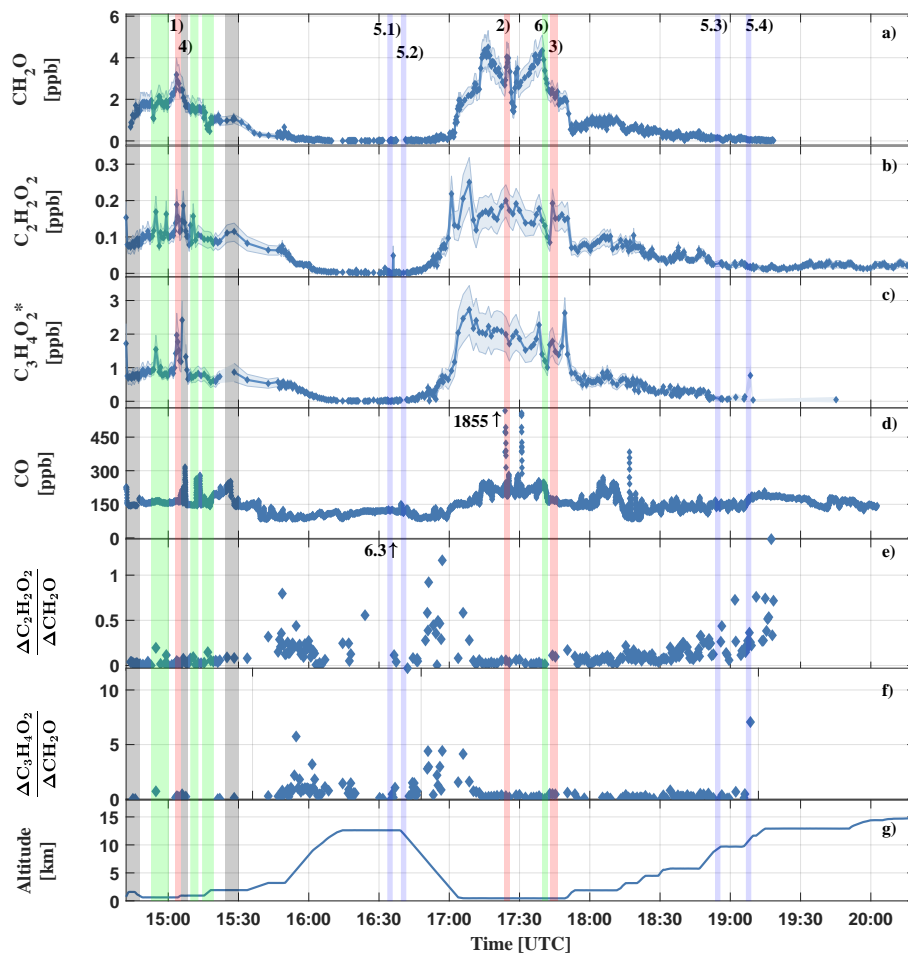


Figure 8. Measured mixing ratios of CH_2O (panel (a)), $\text{C}_2\text{H}_2\text{O}_2$ (panel (b)), $\text{C}_3\text{H}_4\text{O}_2^*$ (panel (c)), CO (panel (d)), inferred $R_{\text{GF}} = \Delta\text{C}_2\text{H}_2\text{O}_2/\Delta\text{CH}_2\text{O}$ (panel (e)), $R_{\text{MF}} = \Delta\text{C}_3\text{H}_4\text{O}_2^*/\Delta\text{CH}_2\text{O}$ (panel (f)), and the height versus time trajectory for the HALO flight AC11 (panel (g)). The shaded blue area in panels (a) to (c) shows the respective measurement uncertainty. All measurements within the Manaus city plume are marked by grey bars (e.g. event AC11-4). Examples for measurements in aged air masses of the upper troposphere are marked in blue (e.g. events AC11-5.1–5.4), and green for the general background atmosphere i.e. tropical forest affected air (e.g. event AC11-6). All measurements of biomass burning plumes are labelled in red (events AC11-1, AC11-2 and AC11-3). The event numbers correspond to the labelling in Table 3 and fig. 7. The colour coding in panels (e), and (g) corresponds to the inferred or of each measurement, in order to emphasize the differences in the gas ratios otherwise not clearly distinguishable due to the logarithmic scale of the y-axis.

during the oxidation of mostly CH_4 and, if available, some residual VOCs, OVOCs, and BVOCs (cf., see fig. 9, panel (e)–c for $\text{C}_2\text{H}_2\text{O}_2$ and panel (d)–d for $\text{C}_3\text{H}_4\text{O}_2^*$), since their photochemical and heterogeneous removal is certainly slower than the CH_2O photochemical lifetime of only a few hours (Frost et al., 2002). In contrast, the largest CH_2O mixing ratios measured

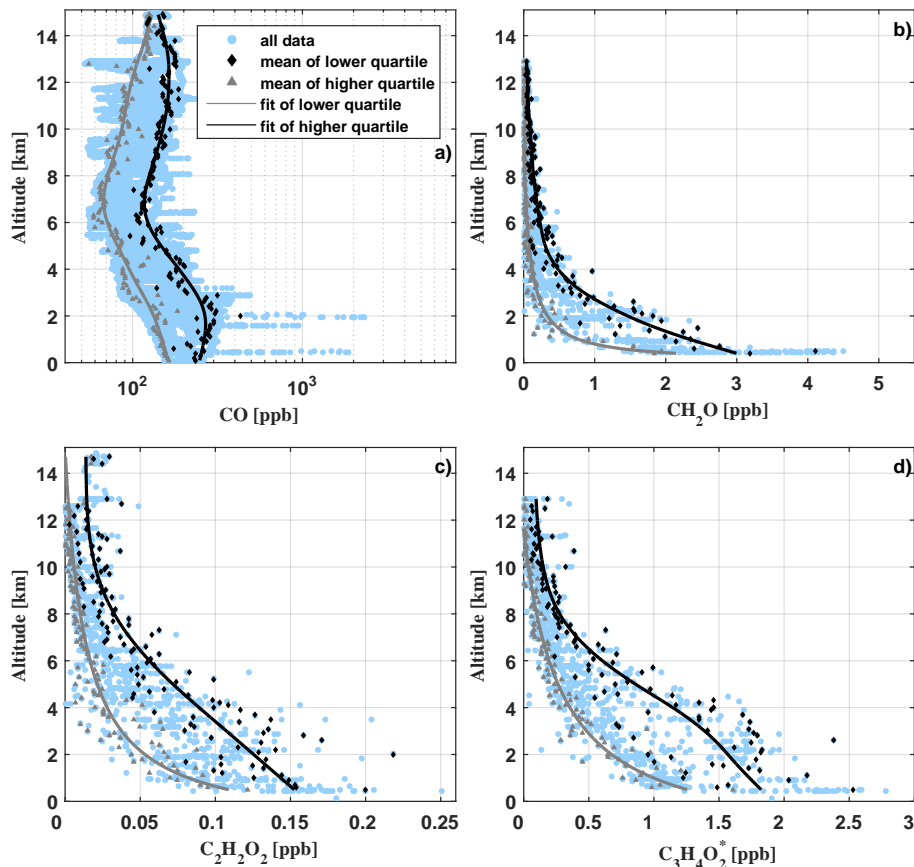


Figure 9. Vertical profiles of CO (panel (a)), CH₂O (panel (b)), C₂H₂O₂ (panel (c)), and C₃H₄O₂^{*} (panel (d)) as measured during flights AC09, AC11, AC12, and AC13 (blue circles). Note the logarithmic scale of the x-axis in panel a. For AC09, there are no CO data available. The grey lines indicate a spline fit (panel (a)) and least squares fits (panel (b) to (d)) through the lower quartile of the data (grey triangles) in 100 m altitude bins. The black line shows lines show corresponding fits through the mean of the upper quartile (black diamonds).

330 over the Amazon at any altitude are appear slightly smaller than the average, and significantly smaller than the maximum
 mixing ratios reported from the joint SENEX aircraft observations of CH₂O and C₂H₂O₂ over North America (Kaiser et al.
 (2015); Chan Miller et al. (2017)).

C₂H₂O₂ mixing ratios range from 85 ppt to 250 ppt below 500 m altitude and decrease in the upper troposphere (12–
 14 km) to mixing ratios from 5 ppt (our detection limit) to about 49 ppt. Close to the ground, our results are comparable
 335 to C₂H₂O₂ mixing ratios found over North America by Kaiser et al. (2015) and Chan Miller et al. (2017), but much larger
 than those measured in pristine air masses of the South Pacific (7–23 ppt) by Lawson et al. (2015). Evidently, besides the
 C₂H₂O₂ formation during the oxidation of BVOCs (Wennberg et al., 2018), a fraction of the near surface and boundary layer
 C₂H₂O₂ is certainly due to direct emission by biomass burning (Zarzana et al., 2018; Andreae and Merlet, 2001b). In the

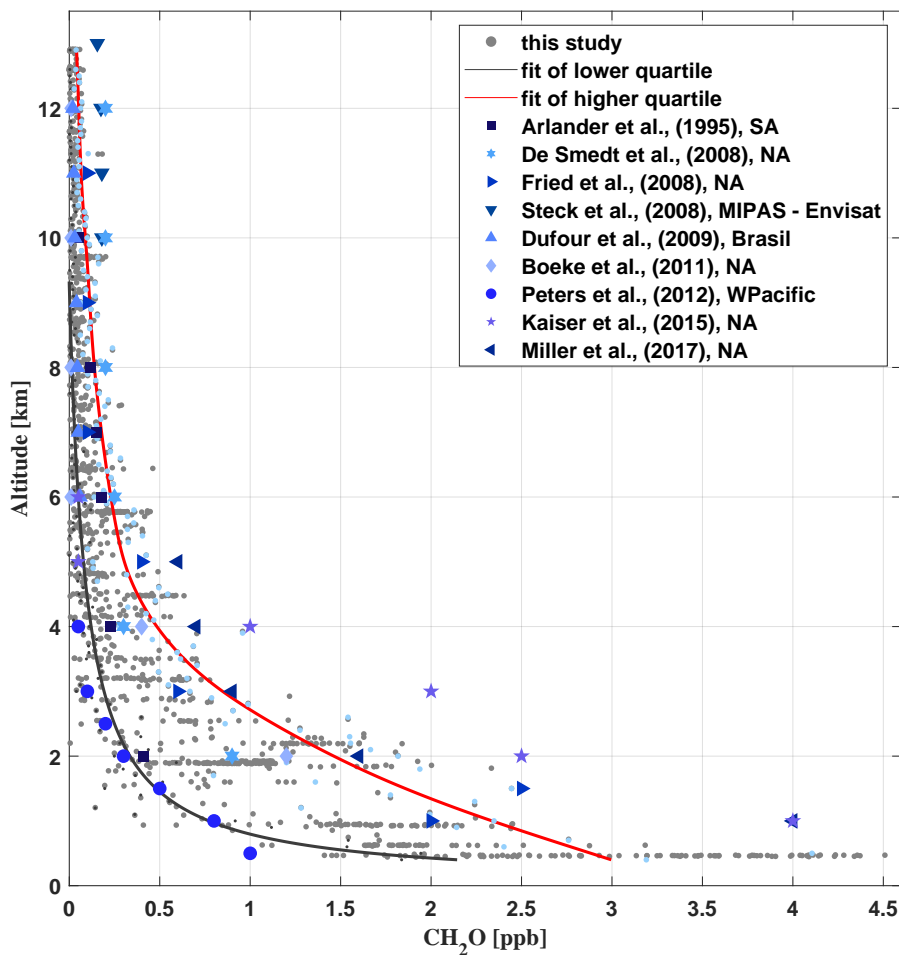


Figure 10. Comparison of different CH_2O measurements available from the literature (Arlander et al., 1995; De Smedt et al., 2008a; Fried et al., 2008; Dufour et al., 2009; Steck et al., 2008; Boeke et al., 2011; Peters et al., 2012; Kaiser et al., 2015; Chan Miller et al., 2017) with those of the present study (blackgrey). The geographical regions of the measurements are Brazil, South America (SA), North America (NA), West Pacific (WPacific) and MIPAS-Envisat measurements covering orbit 8164, $14^\circ \text{ S}/46^\circ \text{ W}$.

middle troposphere, our inferred mixing ratios of $\text{C}_2\text{H}_2\text{O}_2$ are significantly larger than observations during SENEX (which reach to approximately 6 km altitude) and are also larger in the upper troposphere above 6 km when comparing to data
 340 extrapolated from SENEX. Between 6 and 14 km altitude, $\text{C}_2\text{H}_2\text{O}_2$ enhancements of up to ≈ 63 ppt become apparent when compared to either the SENEX data or the binned lower quartile of our data. Such elevated mixing ratios of $\text{C}_2\text{H}_2\text{O}_2$ in the middle and upper troposphere point to an efficient vertical transport of $\text{C}_2\text{H}_2\text{O}_2$ and its precursors VOCs, OVOCs, and BVOCs from their emission sources at the ground (Andreae et al., 2001) or to direct formation from longer-lived VOCs (e.g., phenols)
 345 (Andreae et al., 2001; Taraborrelli et al., 2020). Further, $\text{C}_2\text{H}_2\text{O}_2$ (and $\text{C}_3\text{H}_4\text{O}_2^*$) present at higher atmospheric altitudes may serve as a marker for the formation of ISOPOO (isoprene peroxy radicals), ISOPOOH (oligomer hydroxyhydroperoxides) and

finally IEPOX (isoprene epoxydiols) within the isoprene oxidation chain (Wennberg et al., 2018). In fact, IEPOX mediated SOA formation in the upper troposphere over the Amazon has been reported from observations made within the framework of the ACRIDICON-CHUVA project (Andreae et al., 2018; Schulz et al., 2018).

350 The detection of $C_3H_4O_2^*$, here taken as the sum of methylglyoxal and larger carbonyls as described previously, appears elusive due to the spectral interference among the different species. Weighting of the measured total absorption for $C_3H_4O_2^*$ with the relative absorption cross sections of the inferred $C_3H_4O_2$, $C_4H_6O_2$ (biacetyl), and $C_4C_8O_4$ (acetylpropionyl) (Zarzana et al. (2017), fig. S4) may be indicative of the relative abundance of each species. As in Zarzana et al. (2017), we recommend a weighting factor of 2.0 ± 0.5 by which the inferred $C_3H_4O_2^*$ needs to be divided for indicative $C_3H_4O_2$ mixing ratios.

355 However, we note that the factor of 2.0 ± 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.

Due to the lack of previous atmospheric $C_3H_4O_2^*$ (or $C_3H_4O_2$) measurements, it is more difficult to validate our inferred $C_3H_4O_2^*$ profile (fig. 9, panel (d)). As for the other measured hydrocarbons, the largest $C_3H_4O_2^*$ mixing ratios between 1.2 ppb and 2.8 ppb (mean $[C_3H_4O_2^*]=1.6$ ppb) are found near the ground and within the planetary boundary layer. Below

360 1 km altitude, our results of 0.8 ppb to 2.8 ppb (mean $[C_3H_4O_2^*]=1.5$ ppb) are considerably larger than recently reported $C_3H_4O_2$ mixing ratios (28 ppt to 365 ppt) from a Mediterranean site with intense biogenic emissions and low levels of anthropogenic trace gases (Michoud et al., 2018), as well as measurements at Cape Grim (28 ± 11 ppt) and the Chatham Rise (10 ± 10 ppt) in pristine marine air (Lawson et al., 2015). Therefore, we expect a major fraction of the enhanced $C_3H_4O_2^*$ to be related to the oxidation of BVOCs and biomass burning (e.g., Andreae and Merlet (2001a); Akagi et al. (2011); Stockwell et al. (2015); Zarzana et al. (2017, 2018); Andreae and Merlet (2001b)). Evidence that the former is overall the more relevant

365 process (as compared to direct emissions by biomass burning) in the Amazonian troposphere is also provided by the relatively compact clustering of the inferred $C_3H_4O_2^*$ along the fit of the lower quartile of the data.

5 Discussion

5.1 Vertical profiles and precursor VOCs

370 Above the boundary layer, significant enhancements in $C_2H_2O_2$ and $C_3H_4O_2^*$ mixing ratios above the inferred backgrounds are observed (fig. 9, panels (e) and (d)c and d). After applying a correction factor of 2.0 ± 0.5 to the measured $C_3H_4O_2^*$ mixing ratios as discussed above, methylglyoxal exceeds the inferred glyoxal mixing ratios by up to a factor of five for all measurements. Because of many long flight sections above the remote rain forest, which were to our knowledge at least partly free of fires and plumes, as well as the comparatively different shape of the formaldehyde profile, not all of these enhancements

375 can be attributed to direct emissions from biomass burning.

As their dominant source, isoprene globally accounts for ~~~~~, and of the yearly emissions 67 %, 47 %, and 79 % of the annual sources of formaldehyde, glyoxal, and methylglyoxal (Fu et al., 2008), respectively, leading to their generally correlated rapidly decreasing vertical profiles. As argued by Fu et al. (2008) and Fu et al. (2019), the oxidation of isoprene under low NO_x conditions may be delayed by hours or even several days. This prolonged lifetime combined with the efficient vertical

380 atmospheric transport in the tropics leads to isoprene oxidation above the boundary layer. As a consequence, we suspect the in
situ formation of glyoxal and methylglyoxal and finally formaldehyde from isoprene oxidation to ~~lead~~ contribute significantly
to the observed enhanced mixing ratios in the free troposphere. The methylglyoxal enhancements in the middle troposphere
are approximately five times larger than the observed glyoxal mixing ratios. Molar yields of glyoxal and methylglyoxal from
second and third generation isoprene oxidation combined, are 6.2 % and 34 %, respectively (Fu et al., 2008). Therefore, we
385 expect the in situ formation of methylglyoxal from isoprene oxidation to be approximately five times larger than the respective
glyoxal production. In accordance with our measurements, this should lead to five times larger methylglyoxal mixing ratios
compared to glyoxal in the free troposphere.

~~Despite~~ Besides their common dominant precursor, ~~the secondary~~ additional sources of the gases ~~are different (PAN for~~
~~formaldehyde, acetylene for~~ differently influence their local distribution (mostly combustion processes and oxidation of other
390 biogenic/anthropogenic hydrocarbons in the case of formaldehyde (Lee et al., 1998; Liu et al., 2007; Fortems-Cheiney et al., 2012)
, oxidation of acetylene in the case of glyoxal, and acetone for methylglyoxal (Fu et al., 2008) oxidation of acetone in the case
of methylglyoxal Fu et al. (2008)), and might therefore differently contribute to our measurements. A recent study additionally
discussed the oxidation of aromatics as possible relevant source of atmospheric glyoxal and methylglyoxal (Taraborrelli et al., 2020)
While acetylene is mostly an ~~anthropogenic emitted trace~~ anthropogenically emitted trace gas, acetone additionally has direct
395 biogenic sources. Both gases have a long lifetime of up to 18 and 22 days, respectively (Fu et al., 2008). Therefore, vertically
transported acetylene from ground-based combustion processes might be a further source of the observed glyoxal production in
the free troposphere. While acetone is also emitted in biomass burning processes (one fifth of the total acetone budget (Pöschl
et al., 2001)), an equally large source of acetone emissions is decomposing plant material (10^{-4} g g⁻¹ (Warneke et al., 1999)).
The remaining acetone is to a large part an oxidation product of hydrocarbons and also an oxidation product of isoprene under
400 low NO_x conditions, which are typical for air above rain forests (Warneke et al., 2001). Mean acetone mixing ratios in the
boundary layer above tropical rain forests are on the order of 2 ppb (Pöschl et al., 2001). Besides isoprene oxidation, a fraction
of the observed methylglyoxal enhancements in the free troposphere might therefore be a direct or secondary (through the ox-
idation of hydroacetone) product of acetone oxidation above the boundary layer or a result of longer-lived oxidized aromatics
(Taraborrelli et al., 2020).

405 It is remarkable, that even though formaldehyde, glyoxal, and methylglyoxal have a common dominant source (isoprene)
and sink (photolysis), the relative profile shapes are different. Especially above the boundary layer, the inferred formaldehyde
mixing ratios decrease faster with increasing altitude than the vertical profiles of glyoxal and methylglyoxal do (fig. 9, panel
~~(b)~~ b). It is thus to question whether the relative contribution ~~to the total sink of photolysis and reactions~~ of the different precursor
gases, their sinks due to photolysis and reaction with OH radicals in a low-NO_x, high-VOC, and low-HO_x environment
410 or the different efficiencies regarding the uptake into aerosols or cloud particles may alter the relative profile shapes of the
three species. The water solubility of the gases is largely different ($H^{cp} = 32$ mol m⁻³ Pa⁻¹ for formaldehyde, $H^{cp} = 4100$
mol m⁻³ Pa⁻¹ for glyoxal, and $H^{cp} = 370$ mol m⁻³ Pa⁻¹ for methylglyoxal, see Sander (2015)) and significantly smaller
for formaldehyde than glyoxal. Heterogeneous uptake may therefore not provide an explanation for the relative depletion of
formaldehyde over glyoxal and methylglyoxal in the middle troposphere.

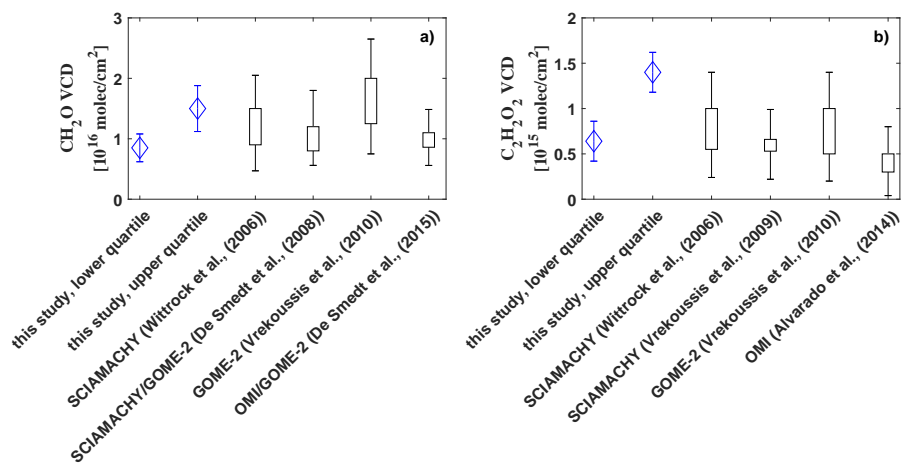


Figure 11. Comparison of the integrated total column amounts/densities of CH₂O and C₂H₂O₂. The vertical bars indicate the range of the observed vertical column amounts as reported in the respective studies. The uncertainty range for Wittrock et al. (2006) and Alvarado et al. (2014) was estimated based on Vrekoussis et al. (2009).

415 5.2 Comparison with satellite measurements

As neither CH₂O nor C₂H₂O₂ have relevant stratospheric sources, the integration of the profiles yields their total vertical column density (VCD). The uncertainty of the integrated profiles follows from the altitude weighted total error of our measurements as displayed in fig. 4. We compare our findings to measurements from GOME (Global Ozone Monitoring Experiment), SCIAMACHY (SCanning Imaging Absorption spectrometer for Atmospheric CHartography), OMI (Ozone Monitoring Instrument), and GOME-2, which combined provide global CH₂O and C₂H₂O₂ observations covering more than a decade (fig. 420 11).

Integration of the CH₂O profiles yields total column amounts/densities of $(0.9 \pm 0.2) \cdot 10^{16}$ molec cm⁻² (lower quartile as plotted in fig. 9) to $(1.5 \pm 0.4) \cdot 10^{16}$ molec cm⁻² (upper quartile), with a mean of $(1.1 \pm 0.3) \cdot 10^{16}$ molec cm⁻² (all data, fig. 11, panel a). Satellite observations generally report enhanced CH₂O VCDs over regions with large biogenic emissions, especially over the Amazon Basin, with maximal enhancements during the dry season. Monthly means of CH₂O VCDs measured by GOME and SCIAMACHY in the years 1996–2007 over the Amazon report maximal enhancements of $1\text{--}2 \cdot 10^{16}$ molec cm⁻² during the dry season and much smaller vertical column densities of $0.8 \cdot 10^{16}$ molec cm⁻² during the wet season (De Smedt et al., 2008b). Our inferred CH₂O vertical column densities based on the lower quartile agree well with their measurements during the wet season, while our integrated profile of the upper quartile lies within the observations during the dry season. Our results agree equally well with SCIAMACHY observations in 2005 over South America with an annual mean CH₂O VCD of approximately $1.2 \cdot 10^{16}$ molec cm⁻² as reported by Wittrock et al. (2006) and also agree with GOME-2 observations, for which Vrekoussis et al. (2010) report CH₂O VCDs of 1.2 to $1.6 \cdot 10^{16}$ molec cm⁻² over the Amazon Basin 430

for the years 2007 to 2008. Finally, yearly averaged CH_2O from OMI and GOME-2 observations over Brazil between 2007 and 2013 by De Smedt et al. (2015) agree with our mean of $1.1 \cdot 10^{16} \text{ molec cm}^{-2}$.

435 The integrated $\text{C}_2\text{H}_2\text{O}_2$ profiles range from $(0.6 \pm 0.2) \cdot 10^{15} \text{ molec cm}^{-2}$ (lower quartile) to $(1.4 \pm 0.4) \cdot 10^{15} \text{ molec cm}^{-2}$ (upper quartile), with a mean of $(1.0 \pm 0.3) \cdot 10^{15} \text{ molec cm}^{-2}$. Based on SCIAMACHY measurements in the years 2002 to 2007, Vrekoussis et al. (2009) report seasonal mean $\text{C}_2\text{H}_2\text{O}_2$ VCDs of $0.5 \cdot 10^{15} \text{ molec cm}^{-2}$ over northern South America in autumn (fig. 11, [panel b](#)). In good agreement with our lower limit, Wittrock et al. (2006) report slightly higher SCIAMACHY $\text{C}_2\text{H}_2\text{O}_2$ observations of approximately $0.6\text{--}0.7 \cdot 10^{15} \text{ molec cm}^{-2}$ over North Brazil for the year 2005. Corresponding to our
440 mean VCD, Vrekoussis et al. (2010) further report average VCDs of $0.5 \cdot 10^{15} \text{ molec cm}^{-2}$ with maximal enhancements of $1 \cdot 10^{15} \text{ molec cm}^{-2}$ based on GOME-2 measurements over South America in the years 2007 to 2008. Observations from OMI yield slightly lower monthly mean $\text{C}_2\text{H}_2\text{O}_2$ VCDs of $0.3 \cdot 10^{15} \text{ molec cm}^{-2}$ (Alvarado et al., 2014). The VCD based on the upper quartile, which is indicative of the large amount of direct glyoxal emissions from various biomass burnings into the boundary layer, is larger than, but still within the uncertainty range of the SCIAMACHY and GOME-2 observations.

445 5.3 R_{XF}^* above the Amazon rain forest

As outlined above, the different air masses probed with the mini-DOAS and AMTEX instrument prevent a definition of emission ratios relative to CO (sect. 2.1 and 2.2). Instead, we ~~infer the use the inferred mixing ratios to calculate the~~ emission ratios R_{GF}^* and R_{MF}^* relative to CH_2O , as often done in remote sensing studies (Fu et al. (2008); Kaiser et al. (2015); Stavrakou et al. (2016); Zarzana et al. (2017, 2018), and others). According to the literature, the background uncorrected emission ratio
450 is defined as

$$R_{\text{XF}}^* = \frac{[\text{X}]}{[\text{CH}_2\text{O}]}. \quad (3)$$

In this study, $[\text{X}]$ is either $[\text{C}_2\text{H}_2\text{O}_2]$ or $[\text{C}_3\text{H}_4\text{O}_2^*]$, as often used in satellite and modelling studies related to hydrocarbon precursors of the studied species (Fu et al. (2008); Kaiser et al. (2015), and others). R_{XF}^* is calculated for each measurement and ~~analysed-analyzed~~ with respect to the measurement altitude (fig. 12, ~~panel (a)-and (b)panels a and b~~).

455 5.3.1 R_{GF}^*

R_{GF}^* mostly remains smaller than 1.0, with a total mean of $\bar{R}_{\text{GF}}^* = 0.35 \pm 0.16$, but reaches maximum values ~~> 5.0~~ during several measurements. Small ratios < 0.05 and large ratios > 1.0 can be observed throughout all ~~analysed-analyzed~~ flights and nearly all altitudes. The comparison with Kaiser et al. (2015) shows, that the inferred R_{GF}^* is notably larger than during most of their ~~measurements over the south-eastern US~~ ~~in situ measurements at altitudes ranging from the ground up to 6 km over the~~
460 ~~southeastern US in June–July 2013~~. Our results are in much better agreement with the R_{GF}^* ~~MacDonald et al. (2012) inferred during measurements over an Asian rain forest~~ ~~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~~. Their R_{GF}^* in the range 0.2 to 0.7 agrees with most of our measurements as well as with \bar{R}_{GF}^* ~~of approximately 0.35~~. From measurements above the Kisatchie National Forest and the Mark Twain National Forest in the south-eastern US, Kaiser et al. (2015) conclude characteristically

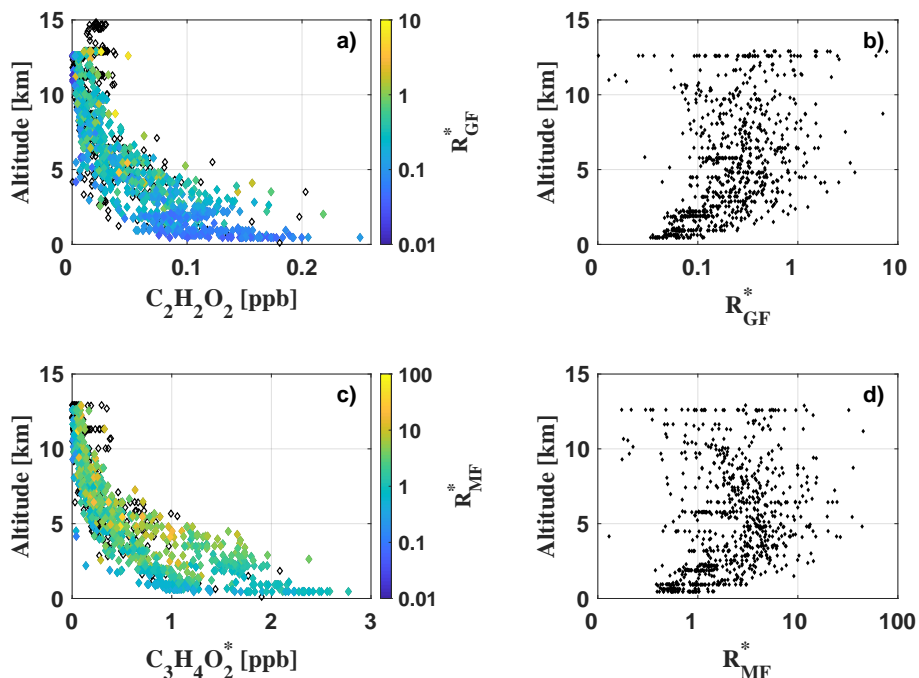


Figure 12. Vertical profiles of $C_2H_2O_2$ (panel (a)) and $C_3H_4O_2^*$ (panel (c)), colour-coded by the ratios R_{GF}^* and R_{MF}^* , respectively, for each measurement during flights AC09, AC11, AC12, and AC13. Black diamonds indicate measurements with missing CH_2O data (recorded with a different spectrometer) and consequently missing ratios. Panels (b) and (d) illustrate the vertical profiles of R_{GF}^* and R_{MF}^* throughout the troposphere. For panels (b) and (d) a logarithmic x-axis has been chosen for a better illustration of the altitude dependence of small R_{GF}^* and R_{MF}^* , respectively.

465 low R_{GF}^* in pristine regions with strong isoprene emissions, while regimes dominated by monoterpene emissions appear to have higher R_{GF}^* . Most of our measurements took place in pristine air masses above the rain forest and far away from any major population centre or other anthropogenic emission sources. Monoterpene and isoprene emissions over the central Amazon were studied in multiple investigations (e.g. Helmig et al. (1998) and Kesselmeier et al. (2000)). All these studies reported generally low mixing ratios of monoterpenes compared to isoprene, which composes 90 % of the total VOC

470 budget in the Amazon (Kuhn et al., 2007). Emissions of monoterpenes, like pinene, on the other hand, alpha-pinene, are at least one order of magnitude smaller than isoprene emissions. Approximately the same relation was found for the total monoterpene emissions (Kuhn et al., 2007; Rizzo et al., 2010). Kaiser et al. (2015) report on approximately 1.2–2.0 times larger $C_2H_2O_2$ yield from α - and β -pinene oxidation with respect to CH_2O . Still, the significant predominance of isoprene emissions over the Amazon clearly compensate for this effect. We conclude that isoprene and not monoterpenes is the

475 dominant precursor of CH_2O and $C_2H_2O_2$ for our observations. Contrary to the measurements of Kaiser et al. (2015) in isoprene rich regimes, the results indicate significantly elevated R_{GF}^* in the troposphere over the Amazon. This is a direct consequence of the much lower CH_2O mixing ratios as compared to their measurements over the south-eastern US.

CH₂O generally does not exceed 1–2 ppb (except for direct measurements in biomass burning or in the Manaus city plume), which is four times less than reported by Kaiser et al. (2015) for pristine air masses over the Mark Twain National Forest (ca. 8 ppb). Our C₂H₂O₂ mixing ratios, on the other hand, are comparable to their findings and typically 100 ppt in the lower troposphere. As a result, we obtain significantly higher R_{GF}^{*} than Kaiser et al. (2015) for the pristine troposphere.

Based on the SENEX observations, Chan Miller et al. (2017) reported mean R_{GF}^{*} of 0.024 below 1 km altitude. Interestingly, Chan Miller et al. (2017) obtained larger R_{GF} of up to 0.06 when NO_x was very low (0.1–0.5 ppb). Even though we are not able to infer NO_x concentrations for all measurements due to instrument failures, we were able to measure NO₂ during all analysed flights. Inferred NO₂ mixing ratios from mini-DOAS measurements were very low during all flights. Mixing ratios above 1 ppb were inferred only in rare cases and exclusively over direct emission sources like Manaus city and in biomass fire plumes. We conclude from these overall low NO₂ mixing ratios, that the measurements during the campaign were generally under very low NO_x conditions. As described in detail by Chan Miller et al. (2017), this could lead to prompt glyoxal formation through isoprene peroxy radicals and thus slightly enhanced R_{GF} compared to observations under high NO_x. Further, from our measurements over Manaus city, we cannot detect any sizeable influence of anthropogenic VOCs on the inferred R_{GF}^{*}. During several low overpasses of the city (< 2 km flight altitude), R_{GF}^{*} did not show any significant difference to measurements distant from anthropogenic emission sources. During the measurements in the city plume, the relative increase of CH₂O and C₂H₂O₂ mixing ratios was similar, leading to consistent R_{GF}^{*}.

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}^{*} remains approximately constant. Both features were previously observed by Kaiser et al. (2015) for altitudes up to 6 km, however less pronounced. Above 10 km, the increase in R_{GF}^{*} between 2–10 km ; our results indicate a slight decrease of appears most pronounced just above the boundary layer (at about 2 km), where CH₂O and C₂H₂O₂ mixing ratios are still significantly above the detection limits. Notably, the correlation of CH₂O and C₂H₂O₂ is larger within the boundary layer than in the free troposphere. When discussing these observations the profile shape of R_{GF}^{*}, one has to keep in mind the very low CH₂O and C₂H₂O₂ concentrations mixing ratios in the upper troposphere and the increasing influence of measurement noise on the inferred mixing ratios. Above 6 km, we observe mean CH₂O and C₂H₂O₂ of only 54 ± 40 ppt and 15 ± 5 ppt, respectively. Still, the increase in between 2–10 appears most pronounced right above the boundary layer at 2, where and mixing ratios are still significantly above the detection limits. Notably, the correlation of and is higher within the boundary layer. In the free troposphere, accordingly, R_{GF}^{*} varies on average by 60 % among the different measurements in within the same altitude range. Following the argumentation of Kaiser et al. (2015), this behaviour can be attributed to the uniform mixing of and within the boundary layer.

5.3.2 R_{MF}^{*}

Generally, R_{MF}^{*} appears approximately 10 times larger than R_{GF}^{*} (fig. 12, panels (e) and (d) c and d). R_{MF}^{*} < 1 are observed only for a minority of the measurements and mostly for background C₃H₄O₂^{*} concentrations. Larger R_{MF}^{*} > 1 are inferred at all altitudes, with a total mean $\bar{R}_{MF}^* = 3.4 \pm 1.6$ and a maximum ratio $R_{MF,max}^* = 45.2 \pm 0.8$. As discussed above for R_{GF}^{*}, the vertical profile of R_{MF}^{*} indicates slightly larger R_{MF}^{*} above the boundary layer and throughout the free troposphere. In the

upper troposphere, R_{MF}^* decreases again, leading to a concave curvature of the vertical profile for small R_{MF}^* , as ~~previously described~~ described above for R_{GF}^* . Several studies were published on the emission ratio of $C_3H_4O_2$ to CH_2O (or CO) in biomass burning plumes (e.g. Hays et al. (2002); Müller et al. (2016); Zarzana et al. (2017, 2018)). To our knowledge, comparable data for air masses of the free troposphere are ~~still missing. As a result, we cannot thoroughly compare to other findings, but focus our analysis on measurements within biomass burning plumes, not yet available.~~

5.4 ~~Normalised~~ Normalized excess mixing ratios in biomass burning plumes and inferred emission factors

During the four measurement flights, a total of twelve biomass burning plume intercepts ~~were~~ was identified based on video imagery (e.g. fig. 7 for events AC11-1.1/1.2 and AC11-3.1/3.2). Most of the plume measurements occurred south of Manaus, and during two extensive flight periods of AC11 and AC13 at altitudes below 2 km. The precise location of all plume intercepts during flight AC11, and the related horizontal averaging kernels of the telescopes are given in fig. 6. As indicated by the backward trajectories, three hours prior to detection all probed air masses moved well within the boundary layer, below 600 m altitude. This time frame more than covers the atmospheric lifetimes of CH_2O , $C_2H_2O_2$ and $C_3H_4O_2$. Consequently, the measured mixing ratios of these gases are a result of fresh emissions at the surface. Each biomass burning plume encounter correlates with significant enhancements in CH_2O , $C_2H_2O_2$ and $C_3H_4O_2^*$ over the background by 13 to 400 %. Based on the backward trajectories combined with video imagery and the short lifetimes of the gases, contributions from other major emission sources (e.g. Manaus city) can largely be excluded. The exact timing, location and altitude of each plume intercept is given in Table 3. As indicated by the numbering in column 1, some of the plumes were probed more than once, giving a total of eight different biomass burning plumes with 12 encounters (further on called events AC11-1.1 to AC13-5). ~~Based on~~ Due to the lack of respective $C_2H_2O_2$ and $C_3H_4O_2$ 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, the mean background mixing ratio of each gas is (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 ~~within the plumes~~. From the resulting enhancements, the normalized excess mixing ratio R_{XF} (or NEMR) is calculated according to

$$R_{XF} = \frac{\Delta[X]}{\Delta[CH_2O]} = \frac{[X_{fire}] - [X_{bkg}]}{[CH_2O_{fire}] - [CH_2O_{bkg}]} \quad (4)$$

with X being either $C_2H_2O_2$ or $C_3H_4O_2^*$. The results for each individual biomass burning event as well as the mean and range of R_{GF} and R_{MF} are given in Table 3.

5.4.1 R_{GF}

R_{GF} ranges between ~~0.024 and 0.11~~ 0.02 and 0.11, with an average of $\bar{R}_{GF} = 0.07 \pm 0.05$. Repeated measurements of the same biomass burning plumes all agree well within the error, indicating the respective plumes were in fact the major emission sources throughout the measurements. The plume AC11-3 (fig. 7) yields the highest R_{GF} of ~~0.097 and 0.11~~ 0.10 and 0.11.

Table 3. Inferred ~~normalised~~normalized excess mixing ratios and emission factors for individual biomass burning events (range and mean). R_{GF} and R_{MF} are given in mole mole⁻¹. The emission factors EF_G and EF_M are in units of g kg⁻¹.

event	time interval [UTC]	location	altitude [km]	R_{GF}	R_{MF}	EF_G	EF_M
AC11-1.1	15:03:19–15:03:51	2.9° S, 60.1° W	0.624–0.632	0.05 ± 0.03	0.09 ± 0.13	0.23 ± 0.13	0.50 ± 0.76
AC11-1.2	15:03:48–15:04:16	2.9° S, 60.1° W	0.615–0.647	0.03 ± 0.02	0.11 ± 0.16	0.16 ± 0.12	0.65 ± 0.94
AC11-2.1	17:21:06–17:23:31	3.6° S, 60.3° W	0.455–0.471	0.06 ± 0.04	0.86 ± 0.39	0.26 ± 0.19	4.96 ± 2.6
AC11-2.2	17:23:31–17:24:48	3.6° S, 60.3° W	0.453–0.470	0.06 ± 0.04	0.66 ± 0.31	0.26 ± 0.18	3.8 ± 2.04
AC11-2.3	17:24:50–17:26:30	3.6° S, 60.3° W	0.452–0.470	0.03 ± 0.03	0.51 ± 0.26	0.16 ± 0.15	2.93 ± 1.68
AC11-3.1	17:43:27–17:44:41	2.9° S, 60.5° W	0.450–0.456	0.11 ± 0.10	1.50 ± 0.60	0.52 ± 0.47	8.64 ± 4.13
AC11-3.2	17:44:43–17:45:52	2.8° S, 60.5° W	0.449–0.454	0.10 ± 0.11	1.30 ± 0.70	0.45 ± 0.52	7.49 ± 4.49
AC13-1	16:33:41–16:34:20	11.0° S, 56.2° W	0.923–0.934	0.04 ± 0.05	1.20 ± 0.60	0.18 ± 0.23	6.91 ± 3.90
AC13-2	16:34:20–16:34:56	11.1° S, 56.2° W	0.921–0.932	0.08 ± 0.07	1.40 ± 0.70	0.37 ± 0.34	8.06 ± 4.55
AC13-3	16:35:39–16:36:18	11.2° S, 56.2° W	0.918–0.929	0.03 ± 0.04	0.76 ± 0.43	0.13 ± 0.17	4.35 ± 2.73
AC13-4	16:37:01–16:37:43	11.2° S, 56.2° W	0.915–0.932	0.05 ± 0.04	0.81 ± 0.43	0.23 ± 0.19	4.67 ± 2.76
AC13-5	16:52:15–16:53:03	11.2° S, 56.2° W	1.849–1.191	0.02 ± 0.02	0.56 ± 0.27	0.11 ± 0.10	3.25 ± 1.77
Range				0.02–0.11	0.09–1.50	0.11–0.52	0.50–8.64
Mean				0.07 ± 0.05	0.98 ± 0.42	0.25 ± 0.23	4.70 ± 2.70

Unfortunately, the plume was not reported in the MODIS fire database. Therefore, we do not know the precise location of the fire and cannot discuss the results with respect to the distance of the aircraft from the plume. The smallest R_{GF} of ~~0.024~~0.02 is found during a measurement with an approximately 1000 m higher flight altitude than during the rest of the events.

Our results are consistent with recent laboratory studies on biomass burning emissions by Zarzana et al. (2018) as well as different field measurements and satellite observations by Chan Miller et al. (2014, 2017); DiGangi et al. (2012); Wittrock et al. (2006) and Zarzana et al. (2017). From laboratory measurements, Zarzana et al. (2018) reported an average R_{GF} of 0.068 for fresh emissions and different kinds of fuels. Without further knowledge on the fuels burned during the observed events, we cannot make firm conclusions on the photochemistry within the fire plumes. While different fuel types may lead to changing emission factors of glyoxal, Zarzana et al. (2018) observed only little variance in R_{GF} for different burning species. The correlation of $C_2H_2O_2$ and CH_2O seems to be consistent for different kinds of fuel. The lack of knowledge of the exact fuels burned in each fire is therefore not an issue when comparing R_{GF} of the different plumes and intercepts. In two older studies, Hays et al. (2002) and McDonald et al. (2000b) report much higher R_{GF} on the order of approximately 2.5 to 3 for *Palmae* and *Poaceae* (Hays et al., 2002) and even up to 4 (McDonald et al., 2000b). Our inferred R_{GF} are at least one order of magnitude lower. In fact, results larger than 1 are only observed for the background-uncorrected R_{GF}^* in the free troposphere.

During recent field measurements over the US, Zarzana et al. (2017) report R_{GF} in the range 0.008 to 0.110. Due to the very nature of ~~airborne~~air-borne plume measurements, we do not know by how much the measurements differ with respect

560 to plume age, air mass origin, atmospheric composition, measurement distance to the plume, etc. Despite the very different atmospheric backgrounds and conditions, our measurements over the rain forest agree well with their findings.

Measurements of an aged biomass burning plume yield slightly smaller R_{GF} of 0.02 to 0.03 (DiGangi et al., 2012). Of all events, event AC13-5 is most likely the oldest plume measured. This is a consequence of the high flight altitude in combination with the distance from the aircraft to the plume during the measurement. AC13-5 has the smallest R_{GF} of only ~~0.024~~0.02,
565 which agrees with the findings of DiGangi et al. (2012). We cannot state by how much this plume measurement is influenced by the general atmospheric background. The air masses in the boundary layer are generally highly polluted with biomass burning emission of different ages. We do not know how much these differently aged emissions influenced our individual plume measurements. Therefore, we cannot draw a distinct relationship between R_{GF} and the plume ages, which, due to the well-mixed condition of the boundary layer most probably varied between several minutes to hours during all measurements.

570 5.4.2 R_{MF}

R_{MF} ranges between 0.09 and 1.50, with an average of $\bar{R}_{MF} = (0.98 \pm 0.42)$. Three of the eight probed plumes yield $R_{MF} > 1$ (both measurements of AC11-3, AC13-1, and AC13-2). All the other plumes yield $R_{MF} < 1$, in the range of 0.09 to 0.86. For event AC11-1, R_{GF} is comparable to the other results, while R_{MF} is significantly smaller than the average \bar{R}_{MF} by approximately a factor of 10. Based on the video imagery, the size of the observed plumes as well as the estimated distance to
575 the aircraft are comparable during events AC11-1 and AC11-3 (fig. 7). Still, they yield very different ~~normalised~~normalized excess mixing ratios. In fact, the largest R_{MF} and R_{GF} are obtained during event AC11-3. Accordingly, the emission of $C_2H_2O_2$ and $C_3H_4O_2^*$ with respect to CH_2O is the highest within this biomass burning plume. Interestingly, this is not connected to the size and quantity of the biomass burning events ~~seen~~monitored by the telescopes. The highest emissions (i.e. the largest plumes) were observed during event AC11-2, where three different large fires were simultaneously detected in a
580 generally hazy atmosphere rich in fresh emissions (fig. 7). These plumes were also recorded by MCD14 on MODIS (fig. 6, red dots in the field of view of event 2.2). Laboratory measurements report R_{MF} approximately between 1 and 2 for different kinds of fuels (Hays et al., 2002). This is the upper range of our observations. Instead of R_{MF} , Zarzana et al. (2018) report the ratio $C_3H_4O_2$ to $C_2H_2O_2$ (R_{MG}) to be on the order of 1.7–2.5 for burning rice straw and different kinds of canopy. Our measurements yield R_{MG} in the range 1–3, with the exception of event AC11-1, where $R_{MG} < 1$ due to the small $C_3H_4O_2^*$
585 mixing ratios. Event AC11-3 yields $R_{MG} = 1$ during both measurements. This reflects the correlated strong enhancement of both gases within the biomass burning plumes.

5.4.3 Biomass burning emission factors

According to Andreae and Merlet (2001b), the biomass burning emission factors for $C_2H_2O_2$ and $C_3H_4O_2^*$ are defined by the ~~normalised~~normalized excess mixing ratio R_{XF} as

$$590 \quad EF_X = R_{XF} \frac{MW_X}{MW_{CH_2O}} EF_{CH_2O} \quad (5)$$

using the molecular weight MW of each species, and the mean emission factor $EF_{\text{CH}_2\text{O}}$ of the reference trace gas CH_2O . As the latter was not measured during the campaign, we use the recent comprehensive compilation by Andreae and Merlet (2001b), which reports $EF_{\text{CH}_2\text{O}}$ with respect to different combustion processes and fuel types. For tropical forest fires, Andreae and Merlet (2001b) inferred mean $EF_{\text{CH}_2\text{O}}=2.4 \pm 0.63$. The resulting EF_{G} and EF_{M} are listed in Table 3 for each biomass burning plume intercept in units of g (target species) kg^{-1} (fuel).
595

EF_{G} ranges from 0.11 to 0.52 g glyoxal per kg of fuel burned with a mean emission factor of $(0.25 \pm 0.23) \text{ g kg}^{-1}$. According to its high R_{GF} , event AC11-3 yields the highest emission factors of 0.52 and 0.45 g kg^{-1} . Five out of the twelve plume encounters yield emission factors of less than 0.2 g kg^{-1} . Corresponding to the largest EF_{G} , Andreae and Merlet (2001b) estimated $EF_{\text{G}}=0.6 \text{ g kg}^{-1}$ for tropical forest fires. In the same study, glyoxal emissions from open burns of agricultural residues were estimated to be approximately 60 % lower with $EF_{\text{G}}=0.23 \text{ g kg}^{-1}$. All biomass burning events encountered during flight AC13 were located between 11.0–11.2° S and 56.2° W. While other parts of the measurement flight were located over rain forest, this region is largely dominated by agricultural activities. EF_{G} of events AC13-1 to AC13-5 ranges from 0.11 to 0.37 g kg^{-1} . Assuming that the biomass burning plumes were dominated by agricultural residues during these measurements, we infer a corresponding mean emission factor $EF_{\text{G}}=(0.25 \pm 0.23) \text{ g glyoxal per kg of open burns of agricultural residues}$.
600
605 The range of EF_{G} further agrees with laboratory measurements by Zarzana et al. (2018), who reported EF_{G} in the range of 0.06 to 0.55 g kg^{-1} depending on the fuel type.

EF_{M} ranges between 0.5 and 8.64 g methylglyoxal per kg of fuel burned, with a mean emission factor of $(4.68 \pm 2.7) \text{ g kg}^{-1}$. For each biomass burning event, EF_{M} is at least twice as high as EF_{G} . The largest EF_{M} were found during flight AC13, i.e. for fires dominated by agricultural residues. Even after ~~applaying~~ applying the correction factor of 2 on the inferred EF_{M} ,
610 the results are significantly larger than reported by Zarzana et al. (2018) from laboratory measurements, who found maximal emission factors of approximately 2 g kg^{-1} for burns of duff. While their absolute EF_{M} are much lower, their results were equally variable with EF_{M} ranging from 0.11 to 2.0 g kg^{-1} .

6 Conclusions

We report on the first simultaneous measurements of CH_2O , $\text{C}_2\text{H}_2\text{O}_2$ and $\text{C}_3\text{H}_4\text{O}_2^*$ over remote and polluted sections of the Amazon. The measurements were performed from on board the DLR HALO aircraft during the ACRIDICON-CHUVA campaign in fall 2014 (Wendisch et al., 2016). The observations took place in the troposphere between 500 m and 15 km altitude, where air masses of different compositions were encountered. These include continental background as well as aged and fresh biomass burning plumes.
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The observed formaldehyde mixing ratios in the lower and free troposphere range from those previously reported over the remote Pacific (Peters et al., 2012) up to those measured over continental North and South America (Kaiser et al., 2015). The lower quartile of the measured mixing ratios appears to result from the oxidation of methane and to a lesser degree of VOCs (mostly isoprene). In the lower troposphere, enhanced formaldehyde mixing ratios have two major contributions: direct emission ~~from biogenic sources or biomass burning~~ g. from biomass burning, and secondary formation during the degradation
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of short-lived VOCs, [like isoprene](#). In the middle and upper troposphere, formaldehyde seems to have more constant sources
625 and sinks than in the lower troposphere. While the sink (mostly photolysis) may not vary significantly with altitude, the
degradation of longer lived VOCs provides a comparably constant source. When integrating our profiles, our observations are
in good agreement with previously inferred formaldehyde VCDs from satellites (De Smedt et al., 2008b; Wittrock et al., 2006;
Vrekoussis et al., 2010; De Smedt et al., 2015).

A good agreement with previous satellite measurements is also found for the lower and upper range of profile integrated
630 glyoxal mixing ratios (Wittrock et al., 2006; Vrekoussis et al., 2009, 2010; Alvarado et al., 2014). Analogously to the presence
of formaldehyde, the lower bound of glyoxal is due to the oxidation of precursor VOCs. Besides direct emissions from biomass
burning and secondarily formed glyoxal from short lived precursors, the oxidation of longer lived precursors like isoprene or
acetone contributes to elevated glyoxal mixing ratios in the free troposphere. [Taraborrelli et al. \(2020\) report in a recent study
on long-lived VOCs like aromatics as a potential additional source of glyoxal in the free troposphere on a regional scale.](#)
635 [Recent findings by Alvarado et al. \(2020\) reveal long range transport of glyoxal and formaldehyde within biomass burning
plumes reaching distances of 1500 km downwind and thus enlarging the assumed local influence of biomass burning events
on the tropospheric distribution of both gases. The time needed to reach such distances is in the order of several days, which
implies the formation of glyoxal and formaldehyde from longer-lived precursors within the plumes.](#)

In agreement with the study of Zarzana et al. (2017), $C_3H_4O_2^*$ mixing ratios generally exceed those of glyoxal by at least a
640 factor of 5 during the majority of the measurements. Yet, the shapes of the upper and lower bounds appear similar to the profile
shape of glyoxal in contrast to formaldehyde, which appears to decline faster above the boundary layer in the low- NO_x , high-
VOC, and low- HO_x environment probed during this study. The compact clustering as well as the smooth decrease of the lower
quartile mixing ratios with altitude indicate the type and sink of the precursor molecules. Apparently, these precursors should
have lifetimes of at least several days, and should either be constantly emitted by the biosphere (e.g. isoprene and acetone) or
645 occasionally during biomass burning (e.g. acetylene, [aromatics](#)) before being vertically transported. R_{GF}^* and R_{MF}^* are found
to increase with altitude due to the more rapid decrease of formaldehyde relative to glyoxal and methylglyoxal mixing ratios.
Again, this [behaviour/behavior](#) expresses the different and changing fractions of the short and long-lived precursors relevant for
the formation of formaldehyde as compared to those of glyoxal and methylglyoxal. In particular, the increasing R_{GF} and R_{MF}
in the middle and upper troposphere require significant sources for both gases which are supposed to result from the oxidation
650 of longer-lived VOCs (Schulz et al., 2018). In fact, since both gases are known to contribute to SOA formation, the elevated
mixing ratios of glyoxal and methylglyoxal in the upper troposphere further lend support to the proposed SOA formation from
products of isoprene oxidation as observed by Schulz et al. (2018); Andreae et al. (2018) and Williamson et al. (2019) over the
Amazon Basin and generally in the tropics.

Our inferred R_{GF} in the range of 2.4–11.2 ($\bar{R}_{GF}=6.5$) for the observed biomass burning events agree well with previous
655 studies, both in the field over North America (Zarzana et al., 2017) as well as in the laboratory fuel study (Zarzana et al., 2018).
It is further in agreement with R_{GF} inferred from satellite measurements (Chan Miller et al., 2014, 2017; DiGangi et al.,
2012; Wittrock et al., 2006). For R_{MF} , we infer a range of 0.09 to 1.5 with $\bar{R}_{MF}=0.98$ (or respectively smaller results when
correcting the $C_3H_4O_2^*$ mixing ratios by a factor of 2.0 ± 0.5), which overlaps with the lower end of the range of normalized

excess mixing ratios previously reported by Hays et al. (2002) for different types of fuels in the laboratory. The presented
660 study as well as the measurements by Hays et al. (2002) indicate a slightly larger R_{MF} than estimated from R_{MG} and R_{GF}
(appr. 0.1–0.5) reported by Zarzana et al. (2018), even though this difference may in part be a result of additional dicarbonyls
included in our retrieval. In fact, when correcting R_{MF} by a factor of 2, our results agree much better to the measurements
by Zarzana et al. (2018). Based on R_{GF} and R_{MF} and average emission factors for formaldehyde estimated by Andreae and
Merlet (2001b), we infer emission factors in the range of 0.11–0.52 ($\overline{EF}_G = (0.25 \pm 0.23) \text{ g kg}^{-1}$) for glyoxal and 0.5–8.6
665 ($\overline{EF}_M = (4.7 \pm 2.7) \text{ g kg}^{-1}$) for methylglyoxal for the probed biomass burning events over the Amazon. Our inferred EF_G
agrees well with the range reported from laboratory measurements (Zarzana et al., 2018). Notably, our EF_M is significantly
larger than found in their study, also when correcting the results for possibly included additional dicarbonyls.

The presented study may be complemented by future studies with data collected during several past HALO missions, i.e.
ESMVal (fall 2012), OMO (over the Mediteranean in summer 2014), EMeRGe (Europe in summer 2017 and Eastern Asia in
670 spring 2018), CAFE (over West Africa/tropical Atlantic in summer 2018), and Southtrac (Southern Argentina and northern
Antarctica in fall 2019), which may provide further information on the role of carbonyls in global atmospheric chemistry.

Data availability. All the data are archived in the HALO data depository (<https://halo-db.pa.op.dlr.de/mission/5>), datasets 6495-6502 (mini-DOAS data), and 3440-3442 (AMTEX CO data). The data are accessible upon signing a data protocol.

Author contributions. TH, MK and KP operated the mini-DOAS instrument and ML and HS performed the AMTEX measurements dur-
675 ing the ACRIDICON-CHUVA campaign. TH wrote the data retrieval software. FK performed the data analysis and wrote the paper with
contributions from ML, KP and HS.

Competing interests. The authors declare that they have no conflict of interest.

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