

Atmos. Chem. Phys. Discuss., author comment AC3
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Reply on RC2

Flora Kluge et al.

Author comment on "Airborne glyoxal measurements in the marine and continental atmosphere: comparison with TROPOMI observations and EMAC simulations" by Flora Kluge et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-416-AC3>, 2022

We are very grateful to the reviewer for his/her comments, to which we react in the following way.

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

Major comments:

- **One of the main concerns in the CHOCHO retrieval is the impact of aerosols, especially for those emissions from biomass burning but also over highly polluted regions. Probably not accounting to aerosols could lead to overestimation of glyoxal from airborne and also satellite observation, and thus more discussion in this direction need to be introduced. Have you evaluated the impact of aerosols to the total error in your retrieval? How much is it?**

AC: For the radiative transfer simulations, multiple regionally and seasonally averaged aerosol profiles are used (based on LIVAS and SAGEII observations, see our response to point 31). The impact of the assumed profile on the glyoxal retrieval (e.g. underestimation of the actual aerosol load in cases of strong local emissions) is quantified by additionally employing an aerosol profile representative for highly polluted aerosol conditions in the radiative transfer simulations (Supplement, Fig. 1, panels c and d). The simulated glyoxal concentrations and VCDs (Supplement, Fig. 1, panels a and b) based on the assumed aerosol for average (AP1) and severely polluted (AP2) conditions are shown below, exemplarily for a research flight conducted partly over the Upper Silesian Coal Valley (high aerosol load) on May 29, 2018. Evidently, the Nadir retrieved VCDs are only moderately sensitive to the employed aerosol profile, which in the case of occasionally local enhanced aerosol may lead to an average deviation in the inferred glyoxal VCDs of up to 20%. The small sensitivity of our Limb retrieved glyoxal concentrations to the assumed aerosol profile is a result of the employed scaling method, which analyses glyoxal relative to a second (scaling) gas of which the detection is equally affected by aerosols.

- **Several glyoxal plumes are identify from biomass burning, but also anthropogenic emissions with four plumes corresponding to high amounts of glyoxal, and thus expected from these specific hot-spots. However, under non**

extreme events, glyoxal detection is low and probably model simulations could correspond more to real glyoxal amounts on average than to those specific scenarios, which could lead to amiss conclusions in this study.

AC: We are not totally sure about the meaning of the reviewer's comment. We are aware of possible deviations of modelled and measured glyoxal (or for that matter also of air- and spaceborne measurements) when observing locally confined emission events. We argue that such discrepancies are mostly a consequence of the moderate spatial resolution of the model as well as missing details in the emission of glyoxal and its precursors as compared to the airborne glyoxal observations. Consequently, we perform the model-measurement comparison separately for identified emission plumes and the background atmosphere (i.e. outside these plumes) and also distinguish this in Fig. 10 of the manuscript (compare lines 704 and following).

- **Although, the authors mentioned that altitude criteria selection of flights is done, not clear reason why the difference between TROPOMI and mini DOAS come from, since both perform similar geometric observation and not difference should be expected between satellite and airborne above the altitude selection.**

AC: Please consider our discussion of the different viewing geometries of air- and spaceborne measurements in the replies to the editor's comments. In order to clarify this point, we added an additional figure to the manuscript (Supplement, Fig. 2).

- **Finally, why the focus is only CHOCHO but not on formaldehyde (HCHO), which is also possible to retrieve with the mini-DOAS system. In addition, it is well known that this species is also emitted from biogenic, anthropogenic and pyrogenic emissions and behave similar to CHOCHO?**

AC: We agree about the detectability and similarities in the spatial and temporal distribution and fate of atmospheric formaldehyde and glyoxal. In fact, they motivated the simultaneous analysis of glyoxal and formaldehyde in our previous study on carbonyl measurements over the Amazon (Kluge et al., 2020, <https://acp.copernicus.org/articles/20/12363/2020/>). However, we would like to emphasise that the present study intentionally focuses on the retrieval of glyoxal and on the inferred science. A general overview over the other related carbonyls is beyond the scope of this study, which is already of considerable length. However, an extensive study on coincident retrievals of formaldehyde (and methylglyoxal) and the analysis thereof is the present subject of ongoing research.

Specific comments:

- **P2, Line 25. 'potentially from sea', would you please clarify in which direction the differences occur**

AC: We changed line 24 to: ...glyoxal producing volatile organic compounds (VOC) from the biosphere (e.g. the Amazon, which is the only region where the model predicts more glyoxal than observed), ...

- **P2, Line 53. Glyoxal lifetime depends on environment conditions like urban or it is similar in all environments?**

AC: In the daytime atmosphere, glyoxal is mainly removed via photolysis and to a lesser degree by oxidation (with OH), or heterogeneous reactions (SOA formation). Generally, with photolysis being the major removal pathway, the lifetime is expected to be similar for a similar illumination in different air masses.

- **P5, Line 145, what is the effect in the glyoxal retrieval due to the low spectral resolution in the visible range?**

AC: Clearly the spectral resolution reduces the differential optical density as compared to a high resolution glyoxal spectrum (e.g. Volkamer et al., 2005). This is indicated in Fig. 3 (Supplement) where we compare this high resolution spectrum of glyoxal with the differential optical density employing a 0.5 nm (e.g. Sinreich et al., 2010) with the 1 nm spectral resolution of the present study. Though notable, the difference in the differential optical density between the 0.5 nm and 1 nm resolution is small (about 10%).

- **P6, Table 1 and Table 2, why in the retrieval of glyoxal from mini DOAS system, different cross-section is used than this used for the satellite retrieval, e.g. Pope and Fry (1997) instead of Mason et al. (2016), what is the impact of this cross-section in the validation?**

AC: Since both liquid water absorption cross sections have comparable spectral resolutions (2 nm and 2.5 nm, see Mason et al., (2016) and Pope et al., (1997)) and are only marginally different in the wavelength range of interest, we kept the absorption cross of Pope and Fry (1997) for the present analysis for comparison reasons with the Kluge et al, 2020 study.

- **P6, Table 2. Why CHOCHO retrievals are in different wavelength? Why not used same spectral range and how glyoxal depends on these changes? Could you quantify it?**

AC: See our responses to point 11.

- **P7, Line 162. Despite that the authors mention that not significantly effect is observed in the NO₂. Is the case for all type of environments? Because previous studies demonstrate that the cross-correlation between NO₂ and CHOCHO is significant under anthropogenic emissions.**

AC: We do not state that absorption due to NO₂ can generally be neglected in the analysis, but that the addition of a second (colder) NO₂ negligibly affects the glyoxal retrieval. However, a (warm) NO₂ cross section taken at temperatures representative for the lower troposphere is included in all spectral retrievals. In the discussion of our glyoxal retrieval scenario, we simply point out that our test retrievals indicated an insignificant sensitivity of the inferred glyoxal to the inclusion of an additional colder (!) NO₂ cross section in the spectral retrievals. Fig. 4 (Supplement) shows two example glyoxal retrievals (excluding and including an additional colder NO₂ cross section) for a Nadir measurement (which should be more sensitive to boundary layer NO₂ than the Limb measurement due to the smaller AMFs/shorter light paths) under elevated NO₂ (simultaneously Nadir detected by mini-DOAS) over the Munich metropolitan area on 7 Aug. 2018. Evidently, the additional cold NO₂ absorption cross section (at 223K) has insignificant impact on the fit quality, the residual structure and the inferred glyoxal.

- **P7, Line 170. As the authors pointed out that the fitting window has been changed to a continue one in comparison to previous study by Kluge et al. (2020) yield to improvements in the spectral residuum and signal to noise ratio, how much large are these improvements (e.g. residual and noise)? What is the relative difference in CHOCHO SCD between previous retrieval and the one used in this study?**

AC: In the analysis, the impact of the wavelength range of the glyoxal retrieval is investigated by applying both suggested fitting windows to all measurements. Fig. 5 (Supplement) indicates that relative to the two discrete fitting windows, the continuous

wavelength range decreases the spectral residual on average by a factor of three, for comparable signal to noise ratios. For measurements in the free troposphere, the resulting dSCDs based on the continuous spectral analysis are systematically larger than those obtained based on the discrete fitting window (Supplement, Fig. 5, panels c and f). This is mainly caused by the larger scatter of the dSCDs around zero when using the discrete wavelength range.

- **P7, Line 178. What different ambient conditions? Is the retrieval of CHOCHO depending on the ambient conditions? If it is the case, why the CHOCHO retrieval should dependent the source producing it?**

AC: Changing ambient conditions (i.e. due to colder/warmer ambient temperatures) do not impact the measurements and spectral retrieval per se, but were considered in the choice of the absorption cross section temperatures employed in the spectral retrieval.

- **P7, Line 179. For off axis DOAS observations the impact of water vapour is significant and cross correlation is more evident for weak absorber such as glyoxal. However, in nadir observation the effect of water vapour in the glyoxal retrieval would be expected rather smaller. Can you quantify this effect in your retrieval and also have you evaluate the dependency of glyoxal retrieval on the water vapour cross-section used?**

AC: Since we report on airborne Nadir and Limb measurements, the line of sight column densities of H₂O are generally much smaller than in off-axis measurements from the ground. Accordingly, retrieval exercises using different H₂O absorption cross sections indicated little dependence on the inferred glyoxal in accordance with the exercises when including and excluding the 7v absorption band of water (see our responses to point 11).

- **P7, Line 188. Would you please write to which location and altitude the reference spectrum corresponds for the different flights?**

AC: As explained on page 7, lines 187 to 190, the reference Fraunhofer spectra are separately selected for each flight. This choice compromises between a) minimal solar zenith angle, b) minimal cloud fraction, and c) maximal flight altitude for the sake of minimizing the amount of glyoxal. Differently to satellite measurements, we use in-flight references for our airborne retrieval, such that the present data set contains 72 different reference spectra, all taken at different locations and altitudes (however always from measurements in the upper troposphere). While the exact locations of each reference can certainly be provided upon request, we fear a table containing all 72 flights would distract from the scientific scope of the paper rather than help the reader.

- **P9, Line 240, Would you please clarify why VCD does not correspond to the total vertical column and only a fraction?**

AC: See the answer to point 3.

- **P10, Line 243. Would you please give a reference or clarification why the 8 km threshold is used for selection of for flight in the comparison?**

AC: See the answer to point 3.

- **P13, Line 338. How large is the spectral variability of mini DOAS system regarding temperature changes in the spectrometer?**

AC: An extensive discussion of the mini-DOAS temperature stability and the temperature dependence of the point slit function can be found in Hünecke (2016) (for download of the

PhD thesis see here <https://archiv.ub.uni-heidelberg.de/volltextserver/22573/>). For low temperatures, the point spread function of the instrument was found to vary by 0.005nm/K. The temperature changes were usually below 1K for flights predominantly performed in the upper troposphere up to several K towards the end of long duration flights within the boundary layer (i.e. at large ambient Temperatures). According to our test measurements in the laboratory, we therefore discarded measurement above a temperature change large than 3K.

- **P13, Line 348. Would you please describe how is applied the empirical correction in case of extreme NO₂ absorption?**

AC: In order to clarify, we added after line 348: 'As described in detail in Lerot et al., (2021), this correction is based on a linear regression fit obtained by a representative sensitivity test for glyoxal measurements at NO₂ > 2·10¹⁶ molec cm².'

- **P14, Line 354. Are aerosols accounted in the (satellite) retrieval?**

AC: See the answers to point 31.

- **P17, Figure 3, The plumes 1.1, 2, etc., are not scaled? The text is a bit confuse, please make clear it.**

AC: The text states: 'All four plumes are not shown in full scale for better comparability with the other profiles.' Instead, for all (truncated) plumes, the maximum glyoxal mixing ratios are given in the legend.

- **P20, Line 495. Is the plume 1.2 also observed from TROPOMI? If yes, how this plume compare to these from Mini DOAS system? How was the evolution of the plume since the fire started? What is the age of the plume?**

AC: The correlation of the two instruments within plume 1.2 is described in detail by Fig. 8, panels c and d. Unfortunately, the latter two questions can't be answered for observations from fast moving instruments deployed on aircrafts or satellites, but only from stationary i.e. ground-based instruments.

- **P21, Line 524. Why glyoxal from Mediterranean Sea are larger than from Amazon rainforest? Normally, glyoxal from biogenic emissions are expected higher than anthropogenic or any other source with exception from biomass burning. Does TROPOMI observe similar behaviour between Mediterranean region and Amazon rainforest?**

AC: As stated in the manuscript, such findings are related to the per-se biased aircraft observations, which are often preferred to probe in particular polluted air masses (e.g. in biomass burning plumes, pollution from larger cities at the coast of the Mediterranean Sea, et cetera rather than background air). On average, biogenic emissions are globally the most important glyoxal source. However, unsurprisingly, local emission plumes (anthropogenic or biomass burning) cause glyoxal enhancements which exceed its biogenic background. Correspondingly, over the Amazon rainforest, the largest glyoxal was observed in biomass burning plumes and not in the general rainforest background (compare Kluge at al., 2020). Equally, the probing of fresh anthropogenic and biomass burning plumes near the Mediterranean coasts yields larger glyoxal than observations in its average biogenic background. Obviously, this pattern is not expected when probing air over the remote Mediterranean or when avoiding local emission plumes. Due to this observation related bias in aircraft studies and since the sampling of TROPOMI (a) is not aimed to selectively probe pollution plumes and (b) is significantly less sensitive to locally confined low lying pollution plumes (as compared to the airborne measurements), the

glyoxal measurements from both instruments in this region can't and should not be compared in a climatological sense but only along the specific flight trajectories.

- **P22, Line 540. Previous studies usually shown low glyoxal values over Europe and the Mediterranean Sea (Lerot et al. 2021, Alvarado, et al 2014, Chan Miller et al 2014), however in this study enhanced values are found over this region. How can be it explained? Could be related to the spatial resolution of satellite observations that low values are observed from Satellite for these regions?**

AC: The cited studies are all from satellite observations, which are better suited to probe 'climatological' fields of pollutants than aircraft. However as stated in the manuscript, the aircraft observations were curtailed (and thus biased) to probe pollution plumes in particular. In this respect, the comment and the questions more point to the problem of comparing the same things. Please inspect again our responses to point 22.

- **P23, Line 594. Why do not use all the flights? Glyoxal is expected be found close to the surface for biogenic and anthropogenic emissions. To what altitude correspond those considered low flying aircraft? Do you expect glyoxal at 7 or 8 km altitude?**

AC: See the answers to point 3.

- **P24, Line 609. Although, to use large grid reduce the noise level in the satellite detection, a smaller grid could lead to more accurate comparison between mini DOAS system and TROPOMI. How the comparison looks using the smallest pixel size of TROPOMI versus mini DOAS system for large glyoxal plumes?**

AC: As stated in the manuscript, individual TROPOMI measurements of glyoxal at low pollution are not very meaningful due to the large noise (for details see the answer to point 29).

- **P24, Line 611. What is the delta time between observations (TROPOMI versus mini DOAS)? There is any criteria for it?**

AC: Since the mini-DOAS flight time varies daily and the TROPOMI overpass time depends on the latitude (13:30 LT equator crossing time), the delta time varies for the individual research flights. During some measurements, both overpasses occurred within minutes, while for others the measurements are some hours apart (≤ 4 h due to the available daylight and the typical timing of individual flights). Consequently, we do not expect both sets of observations to strictly correlate when observing locally confined emission events and for such comparisons the measurement times are indicated in the legend. (e.g. Fig. 8 of the manuscript).

- **P24, Line 619. 3.2×10^{14} variability correspond to the standard deviation?**

AC: All uncertainty ranges are given as median absolute deviation.

- **P27, Figure 8a. Please make more visible the legend for TROPOMI and mini-DOAS or move outside of figure.**

AC: Fig. 8, panel a has been changed accordingly.

- **P28, Figure 9. Although the good consistency between both data sets, the TROPOMI present more negative values than mini-DOAS. Do you know why is the case?**

AC: For individual measurements the TROPOMI retrievals are considerably more noise affected than those made from the aircraft (by a factor of ~ 6 , for details see our response the comments of the editor). In consequence, the satellite measurements are more strongly affected by statistical scatter than the aircraft measurements, which for very low glyoxal leads to relatively more negative results.

- **P29, Line 685. Has the missing of additional NO₂ cross-section impact in the mismatching between TROPOMI and mini-DOAS over these polluted region?**

AC: See the responses to point 10 and Supplement, Fig. 4.

- **P29, Line 687. How is correct for aerosols in the TROPOMI and mini-DOAS retrievals?**

The McArtim radiative transfer model used for the mini-DOAS retrieval accounts for aerosols by including an average, regionally characteristic aerosol profile obtained by LIVAS (Amiridis et al., 2015) and the Stratospheric Aerosol and Gas Experiment II (SAGE II). The dependency of the retrieval on this profile is described in point 1 and Supplement, Fig. 1. The TROPOMI retrieval discards observations affected by dense aerosols and clouds by applying a cloud filter (effective cloud fraction below 20%, compare Lerot et al., 2021). In agreement to the mini-DOAS aerosol sensitivity discussed in question 1, this may lead to an increased uncertainty of the air mass factor in the order of 15% for measurements e.g. affected by strong biomass burning plumes (Lorente et al., 2017).

- **P30, Line 731. Despite the large underestimation from the model, the variability of glyoxal from mini-DOAS is large, which also could lead to miss interpretation of the figure. For those days where the glyoxal variability is large. To what is it associated? Seems to be that TROPOMI (figure 9 vs figure 10) observations match better to the model than the mini-DOAS. How is it explained?**

AC: The larger variability in glyoxal for the airborne measurements is most likely due to glyoxal emissions and glyoxal secondary formation, both of which are not captured in detail by the model. Likewise, as stated in the manuscript, the satellite has difficulties to detect glyoxal plumes of limited vertical extent (and hence with a relatively small contribution to the total atmospheric VCD) as well as to detect faint glyoxal plumes over surfaces of low albedo. It is not very astonishing that the aircraft may provide a more detailed and comprehensive (spatially but not temporally resolved) picture of glyoxal in the atmosphere than the satellite or model are able to provide.

- **P34, Line 817-825. Despite that different plumes are observed and associate to specific events some of them present very high glyoxal amounts, however not for all fire events. Are those plumes observed similar spatially distributed? The amount of glyoxal depends on the precursor emitted from the fire or the type of vegetation? The altitude at which the plumes from fire are injected in the atmosphere play a role in the interpretation from fire emissions?**

AC: In part, we concur with the statements of the reviewer (see our responses to point 32). However, the reviewer and the reader should consider that the present airborne measurements were not specifically designed to monitor glyoxal in different biomass burning plumes (contrary to those for example presented in Kluge et al., 2020) but rather were made within the frameworks and objectives of the different research missions. In this respect, the questions of the reviewer need to be tackled by more dedicated missions in the future.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2022-416/acp-2022-416-AC3-supplement.pdf>