

Atmos. Chem. Phys. Discuss., author comment AC1
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Reply on RC1

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-AC1>, 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).

- **Abstract, line 16: remove "over days"**

AC: We changed line 16 accordingly to: 'Our observations of glyoxal in these aged biomass burning plumes, ..'.

- **Abstract, line 28: suggest "mixture" rather than "cocktail", which is colloquial**

AC: We changed line 28 accordingly to: '...from the degradation of the mixture of...'.

- **Lines 60-62: Please add the Washenfelder et al. reference for measurements in Los Angeles. Washenfelder, R.A., et al., The glyoxal budget and its contribution to organic aerosol for Los Angeles, California during CalNex 2010. J. Geophys. Res., 2011. 116: p. D00V02.**

AC: We added the suggested publication.

- **Line 133: "or briefly" appears to be out of place and likely not intended**

AC: We changed line 133 to: '...the collisional complex O₂-O₂ (further on called O₄; ...)'.

- **Line 191 and following paragraph: Specify the integration time associated with the LOD for the glyoxal dSCD or mixing ratio.**

AC: Since the statistical noise is given by the number of collected photons (N_{PH}), for sufficiently large N_{PH} the measurement noise should be dominated by the read-out noise. At the same time, increasing N_{PH} also increases the spectral integration time and hence enlarges the spatial resolution of the measurement along the flight track of the (moving)

aircraft. Measurements prior to the field deployment of the instrument indicate that an optimal compromise of the photoelectron shot noise, read-out noise, and resolution is obtained when accumulating 100 read-outs at 60% saturation and 300ms exposure time each. In order to clarify, we added in line 191: 'Based on an exposure time of 300ms, a saturation of 60%, and 100 added readouts (30s integration time), the mini-DOAS detection limit for glyoxal...'

- **Line 204: Remove extra parentheses**

AC: We corrected line 204 accordingly to: '...correction factors $\alpha_{x,j}$ and $\alpha_{04,j}$ to quantify...'

- **Line 320: Should biogenic influenced air be on this list? Is this part of pristine continental?**

AC: We are not totally sure about the reviewer's comment, since the paragraph following line 318 exclusively addresses air masses predominately affected by anthropogenic pollution.

- **Line 348: Is the nature of the empirical correction of CHOCHO at high NO₂ explained in Lerot 2021? Is it possible to summarize briefly here?**

AC: The empirical correction of the TROPOMI glyoxal retrieval for strong NO₂ is described in detail in Lerot et al., (2021), section 3.1.2. 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 > 2x10¹⁶ molec cm².'

- **Line 394: Why are direct emissions of glyoxal from biomass burning excluded?**

AC: For the comparison, an EMAC set-up has been used that represents recent

EMAC studies focusing on up-to-date VOC photochemistry. Direct biomass burning emissions of glyoxal were not included in these set-ups so far. To be in line with those studies, we also did not include these biomass burning emissions in the present comparison. An optimised EMAC set-up, which also includes direct biomass burning emissions of glyoxal, is the focus of our companion paper by S. Rosanka, which is under preparation.

- **Table 3: Values are listed as median with standard deviation – should this read mean and standard deviation? Is there a reason for using a median rather than a mean in combination with a standard deviation. Would percentiles be more appropriate, and if so, is the glyoxal in each region normally distributed?**

AC: We replaced the standard deviation by the median absolute deviation throughout the manuscript in order to use an internally consistent statistical measure.

- **Line 488: The large emission of isoprene is associated with the data from South East Asia but not the Amazon basin?**

AC: Yes. For clarification, we changed line 488 to: '...a rural region of South-East Asia (up to 1.6 ppb; Mac Donald et al., (2012)). There, large emissions of isoprene were suspected to cause these large glyoxal concentrations'.

- **Line 562-564: Min et al. also report airborne glyoxal over the Eastern U.S. that can be listed here. Min, K.E., et al, A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor. Atmos. Meas. Tech., 2016. 9(2): p. 423-440.**

AC: We added the suggested publication.

- **Figure 8: Figure is rather difficult to read and would benefit from an overview map identifying the locations of each of the different examples. The insets in the individual figures do not have sufficient reference to understand where each images it taken easily. The labels, (a), (c), (e) and (f) are quite difficult to see.**

AC: We agree and adjusted the insets in Fig. 8, panels a, c, f in order to provide a better reference to the geographic location of each measurement and shifted the panel labels for better visibility.

- **Line 686-688: Measurement noise that leads to negative glyoxal values implies that there is also noise that leads to larger positive values than are actually present in the atmosphere. Inclusion of the positive noise with omission of the negative noise then biases the model – measurement subtraction in Figure 10. Does the one-sided omission of noise bias this comparison? If so, by how much? If not, the authors should justify.**

AC: Each single measurement is affected by a statistical uncertainty, such that n repetitions of the measurement under equal conditions would lead to a normal distribution around the mean value x . Due to the relatively larger uncertainty of the measurements of small as compared to those of large glyoxal concentrations, the relative width of this distribution is expected to be larger for small glyoxal than for large glyoxal observations. For low glyoxal, the respective scatter around the mean may therefore cause negative values in the retrievals. While such negative retrievals are clearly caused by statistics, for large glyoxal there is no robust method to differentiate between statistically overestimated glyoxal (relative to the mean value) and the actual glyoxal. Therefore, in comparison to model simulations which do not produce negative values, for statistical consistency in the two sets of samples the negative retrievals are discarded (Supplement, Fig. 1, black) rather than to keep them in the analysis (Supplement, Fig. 1, red). The comparison of both approaches however indicates that including/excluding negative measurements causes only minor changes to the results, which are all within the uncertainty of the given median differences of the observations and the model (Supplement, Fig. 2).

- **Line 705: Should this read overestimated (not underestimated) emissions of long lived precursors?**

AC: We agree, that the much larger simulated than observed glyoxal in the boundary layer and the free troposphere indicates overestimated rather than underestimated concentrations of longer-lived glyoxal precursors. We consequently changed 'underestimated' to 'overestimated'.

- **Line 800: Glyoxal may also be a product of multi-generation biomass burning oxidation rather than simply long-lived precursors.**

AC: For clarification, we adjusted line 823-824 to: '..., the glyoxal detected in these aged biomass burning plumes was necessarily secondarily formed from direct or multi-generation oxidation of yet unidentified longer-lived VOC precursor species (e.g. benzene, acetylene, or aromatics), which were co-emitted during the wildfires.'

- **Line 805-809: The biomass burning source is a potential explanation for the tropical oceanic glyoxal, but it would have a very different vertical distribution than a surface glyoxal source. To what extent are the vertically resolved data from this analysis consistent with either source?**

AC: To clarify, we added after line 812: 'This finding is supported by the inferred vertical glyoxal profiles over the different marine regions. When comparing the vertical glyoxal profiles above the tropical Atlantic to those over the mid- and high-latitude Atlantic, the relative enhancement of glyoxal in the tropics appears restricted to the tropical marine boundary layer. At higher altitudes, the glyoxal profiles over different regions of the Atlantic are similar (see table 3). This finding strongly points to a marine glyoxal source in the tropics rather than long-range transport of glyoxal and its precursors from terrestrial emissions. If the latter process was the dominant glyoxal precursor in the observed marine air masses, elevated glyoxal would also be expected at higher altitudes and latitudes, and not exclusively in the tropical boundary layer.'

Bibliography

Lerot, Christophe, et al. "Glyoxal tropospheric column retrievals from TROPOMI – multi-satellite intercomparison and ground-based validation." *Atmospheric Measurement Techniques* 14.12 (2021): 7775-7807.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2022-416/acp-2022-416-AC1-supplement.pdf>