

Interactive comment on “Reassessing the ratio of glyoxal to formaldehyde as an indicator of hydrocarbon precursor speciation” by J. Kaiser et al.

Anonymous Referee #2

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This article presents a very useful and careful analysis of glyoxal and formaldehyde data from the SENEX campaign. The campaign is especially well suited for scientific purposes as it covered a wide range of different environments (in terms of isoprene, monoterpenes, AVOC, NO_x). Large discrepancies were found in most previous studies regarding the ratio of glyoxal-to-formaldehyde (R_{GF}). The present study contributes to reduce these inconsistencies and provide interesting clues as to the possible reasons for the seen variations in this ratio. The articles also rightfully shows that the ratio is not well suited to unambiguously constrain anthropogenic vs. biogenic contributions. Interestingly, a relatively good agreement is found between the HCHO-CHOCHO rela-

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tionship from satellite and from in situ (correlation and slope), leading to encouraging conclusions regarding the usefulness of satellite data.

Major comments

1) As pointed out in the paper, the satellite RGF is not well correlated with in situ. The reason given for this discrepancy is the seasonal averaging of the satellite data. When looking more closely, however, some areas such as the Kisatchie forest known to emit monoterpenes, causing high RGF according to SENEX data (as discussed in the manuscript) are not associated to high RGF in satellite data. I believe quite likely that such discrepancy reflects the uncertainties in the measurements, especially from the satellite. The OMI errors deserve more discussion. It is very encouraging to see a better consistency between satellite and in situ R_{GF} data compared to previous studies, but it should be acknowledged that the sources of error for the measurements (especially spaceborne) are plentiful (low signal to noise, interferences from other compounds).

2) Please cite, and compare your results with the study of Lee et al. (1998) which also provided vertical profiles of formaldehyde, glyoxal and other OVOCs over a BVOC-rich area in the Southeast US. Please provide a plot of the mixing ratios of HCHO and CHOCHO instead of (or in addition to) the profiles given in molec/cm³ (Fig. 8). This would facilitate comparison with previous studies. The Lee et al. study also found slightly higher R_{GF} values in the FT compared to the BL. The possible source for the apparent additional source of glyoxal in the FT is unknown, as pointed out in this manuscript, but it has been hypothesized that the heterogeneous oxidation of aerosols might release glyoxal and other OVOCs, as a possible explanation for high CHOCHO in the FT over the Tropical Pacific (Volkamer et al., 2015). The ozonolysis of fatty acids has indeed been found to be a source of glyoxal and other compounds (Zhou et al., 2014).

Minor comments

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Section 2.2, p. 6244: Provide some discussion of the uncertainties in the satellite retrievals

p. 6246, line 2: which monoterpenes are emitted by longleaf pines? Frankin and Snyder (1971) mention alpha-pinene and 1-pinene, but there should be more recent studies. This is relevant as there might possibly be large differences between the glyoxal yields of different monoterpenes.

p. 6248, l. 6: "Isoprene is still likely the dominant OVOC precursor": true, but aren't there means to prove that hypothesis?

p. 6248, l. 14-16: Yes, ISOPROOH can interfere with MVK+MACR measurement, but this does not weaken the argument that oxidation occurs faster in the plume, since ISOPROOH is also isoprene oxidation product.

p. 6249-6250 (Section 3.4) and Table 2: Are the AVOCs of Table 2 the only significant contributions to CHOCHO (not mentioning CH₂O)? What about C₂H₄, C₂H₂, ...?

Minor/technical remarks

p. 6245, l. 26 'On both the 10 June and 25th flights" is awkward, please rephrase.

p. 6248, l. 21: insert "are" after "in-plume"

p. 6249, l. 5: insert "%" after (2.2 ± 0.2)

p. 6249, l. 14-16: Low-NO_x isoprene oxidation is not well understood also (a fortiori) for glyoxal formation, not just CH₂O and OH.

p. 6252, l. 13-16: the sentence "In general, profiles... is less" is awkward. You could e.g. remove the two last words.

p. 6253, l. 13: the year should be 2014 for Gonzalez Abad.

p. 6254, l. 18: please insert "broadly" before "in agreement for the two platforms" given the reservations outlined above.

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References

Frankin, E. C., Snyder, E. B.: Notes: Variation and Inheritance of Monoterpene Composition in Longleaf Pine, *Forest Sci.*, 17, 178-179, 1971.

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Volkamer, R. et al., Aircraft measurements of bromine monoxide, iodine monoxide, and glyoxal profiles in the tropics: comparison with ship-based and in situ measurements, *Atmos. Meas. Tech. Discuss.*, 8, 623-687, 2015.

Zhou, S., Gonzalez, L., Leithead, A., Finewax, Z., Thalman, R., Vlasenko, A., Vagle, S., Miller, L. A., Li, S.-M., Bureekul, S., Furutani, H., Uematsu, M., Volkamer, R., and Abbatt, J.: Formation of gas-phase carbonyls from heterogeneous oxidation of polyunsaturated fatty acids at the air-water interface and of the sea surface microlayer, *Atmos. Chem. Phys.*, 14, 1371-1384, doi:10.5194/acp-14-1371-2014, 2014.

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