Reponse to 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

We thank the referee for the valuable comments. The original comments are shown in italicized black, while responses are provided below in blue.

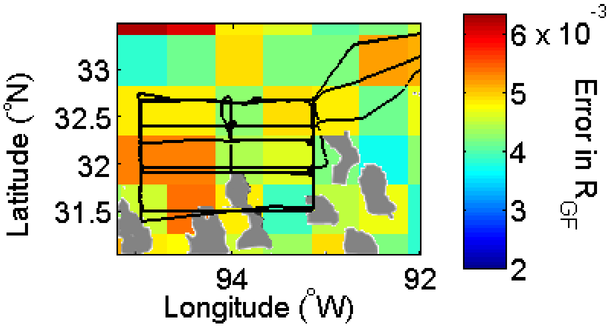
Major comments

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 RGF 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).

The sources of errors in satellite measurements are numerous, including uncertainties in absorption cross sections, the computation of the air mass factor, instrumental uncertainty (e.g., wavelength calibration), potential interferences from other compounds, and low signal to noise. However, seasonal averaging helps to reduce these errors. Assuming a 15% systematic uncertainty and following the formulation thoroughly explained in Vrekoussis et al. (2010), (section 4.3.1), the average error in satellite R_{GF} over the SE US is 0.005, which is 18% of the average R_{GF} value observed in this region.

This is now discussed in section 2.2.

The error calculated for the pixel over the Kisatchie forest (0.0047) is not larger than errors in other pixels (figure at right: flight track is shown in black, forest in grey). The reviewer is correct that at this scale, pixel-to-pixel variation in R_{GF} is mostly associated with noise. Therefore, the retrievals shown here cannot distinguish the local influence of the forest.



This is now discussed in section 3.5

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 RGF 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).

We now include a quantitative comparison of our measurements and the Lee et al. (1998) measurements in section 3. Figure 8 has been remade to show HCHO and CHOCHO in units of ppb. Comparison with R_{GF} vertical profiles observed by Lee et al. (1998) and Li et al. (2014) is now included in section 3.5. Section 3.5 also now mentions the possibility of heterogernous oxidation of aerosols as a CHOCHO source in the F.T.

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

See response to major comment #1.

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.

We now cite a more recent study which details the relative emissions rates of speciated monoterpenes from longleaf pines (*Pinus palustris*). The emission rate of β-pinene is the largest, approximately 30% greater than the α-pinene emission rate. All other monoterpenes emissions are at least an order of magnitude lower (Geron et al., 2000). The modeled relative abundance of HCHO and CHOCHO from the oxidation of α-pinene and β-pinene is included in Table 2.

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

Proving this requires modeling the complete HCHO and CHOCHO budgets, which is beyond the scope of this work. However, we now state that isoprene is a much larger source of OH reactivity than anthropogenic VOCs. This strongly supports our conclusion that isoprene is likely the largest source of both HCHO and CHOCHO.

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

If ISOPOOH creates a positive bias MVK+MACR measurement, the artifact would be larger in the low-NO_x areas, artificially increasing the (MVK+MACR)/isoprene ratio observed outside of the plume. Because (MVK+MACR)/isoprene is higher inside the plume, any interference would not affect the conclusion that oxidation occurs faster in the plume. This is now stated in the manuscript.

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, ...?

While ethene and ethyne are not expected to contribute significantly to the HCHO and CHOCHO budgets, they are now included in Table 2 and discussed in section 3.4. By providing results for increasing length of alkane (ethane to butane) and also bond order (ethane to ethyne), we provide one example of the effect of precursor structure on resultant R_{GF}.

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-NOx 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.

We thank the reviewer for the careful reading. All minor/technical remarks have been addressed.

References:

Geron, C., Rasmussen, R., Arnts, R. R., and Guenther, A.: A review and synthesis of monoterpene speciation from forests in the United States, Atmos. Environ., 34, 1761 1781, 10.5194/acp-5-1053-2005, 2000.

Lee, Y. N., Zhou, X., Kleinman, L. I., Nunnermacker, L. J., Springston, S. R., Daum, P. H., Newman, L., Keigley, W. G., Holdren, M. W., Spicer, C. W., Young, V., Fu, B., Parrish, D. D., Holloway, J., Williams, J., Roberts, J. M., Ryerson, T. B., and Fehsenfeld, F. C.: Atmospheric chemistry and distribution of formaldehyde and several multioxygenated carbonyl compounds during the 1995 Nashville/Middle Tennessee Ozone Study, J. Geophys. Res., 103, 22449–22462, 10.1029/98jd01251, 1998.

Li, X., Rohrer, F., Brauers, T., Hofzumahaus, A., Lu, K., Shao, M., Zhang, Y. H., and Wahner, A.: Modeling of HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD2006 campaign, Atmos. Chem. Phys., 14, 12291-12305, 10.5194/acp-14-12291-2014, 2014.