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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 27 March 2015

The manuscript "Reassessing the ratio of glyoxal to formaldehyde as an indicator of hydrocarbon precursor speciation" by Kaiser et al. reports their high time-resolution airborne measurements of HCHO, CHOCHO, NOx, VOCs, etc. over different areas in the southeast United States. By analyzing the variation of CHOCHO to HCHO ratio (R_{GF}) towards the change of precursor VOCs, Kaiser et al. concluded that R_{GF} is not a reliable diagnostic of anthropogenic VOC emissions for the investigated areas. In addition, the authors stated that the updated OMI CHOCHO data can provide better agreement between satellite and in-situ R_{GF} observations. In general, the manuscript presents a valuable dataset of spatially resolved HCHO and CHOCHO measurements

and provides further insights on the usefulness of R_{GF} in addition to previous studies. I recommend the publication of the manuscript after my following comments have been addressed.

General comments

The conclusion that the updated OMI CHOCHO data can provide better agreement between satellite and in-situ R_{GF} observations is based on the comparison between the 2007 OMI data to the 2013 in-situ data. However, the time difference between the two datasets is so large that many things (e.g., VOC emissions, NOx levels, oxidation capacity / OH level) can change during the long time period. These changes could result in different concentrations and spatial distributions of HCHO and CHOCHO in 2013 than in 2007. Consequently, R_{GF} may not be the same in the two years. If it is possible, I strongly suggest the authors to use 2013 OMI data for this manuscript. Otherwise, the authors should explicitly explain why the R_{GF} derived from OMI observations are similar in the summer of 2007 and 2013. A figure illustrating the change of emission patterns of AVOCs, BVOCs, NOx, CO, etc. would be helpful.

Specific comments

Line 6, Page 6239: "the oxidation products" → "HCHO and CHOCHO".

Line 17 – 19: This conclusion is valid only if the points described in the general comments have been addressed.

Line 19 – 21, Page 6239: I think rationale behind this conclusion is not well explained

in the manuscript. What kind of other measurements are needed? How can the diagnostic by R_{GF} been improved by these measurements?

Line 14, Page 6240: Do alkenes include isoprene and monoterpenes? Probably it is better to use "particularly alkenes, aromatics, isoprene, and monoterpenes".

Line 3, Page 6242: "CHOCHO vcds" → "CHOCHO vertical column densities (Ω_V)". To avoid any confusion, I suggest to use the same symbol for vertical column density as that used in satellite retrievals.

Line 7, Page 6244: "slant columns (Ω_S)" → "slant column densities (Ω_S)".

Line 10, Page 6244: "vertical columns (Ω_S)" → "vertical column densities (Ω_V)".

Section 2.2, Page 6244: Please add description on the time period of the OMI data used in this study. It should also mention that the used OMI data are averaged data over this time period.

Line 5, Page 6245: I understand that the term OVOC in this manuscript only refers to HCHO and / or CHOCHO. Since the normally used OVOC contains more species, the authors should make a clear statement on the species included in their defined OVOC.

Line 7, Page 6245: Can the authors mark the "isoprene volcano" in Figure 1?

Line 8, Page 6245: What does the "background" refer to? Does it mean regions dominated by BVOC emissions? I suggest to reformat this sentence so that the

meaning of "background" is clearer.

Line 9 – 10, Page 6245: I suggest to mark the location of these cities in Figure 1, so that the outflows of the city can be easily identified.

Line 22 – 24, Page 6245: This sentence is difficult to understand. For comparison between observations in different days, the effect of diurnal variation can be minimized by using data obtained at similar time of the day. However, for observations in an individual day, how to minimize this effect?

Line 26, Page 6245: "On both the 10 June and 25th flights," → "During flights on both 10 June and 25 June,".

Line 10 – 20, Page 6246: The R_{GF} on 25 June is in general higher than that on 10 June. Is this difference also caused by the incursion of airmass from free troposphere? In a later section, the authors described that R_{GF} changes with altitude. Therefore, I think it is also worth to mention, on 10 and 25 June, whether the R_{GF} for a certain location is obtained at similar flight altitude.

Line 22, Page 6246: Please specify the major wind direction before using the term upwind.

Line 24 – 25, Page 6246: Which type of VOC is dominant in terms of OH reactivity? BVOC or AVOC?

Line 25, Page 6246: CO_2 data is not shown in Figure 4.

Line 9 – 11, Page 6247: Please add the specific references. As far as I can see, not all literatures in Table 1 support this argument.

Line 11 – 14, Page 6247: To be consistent with the occurrence in the following text, I suggest to exchange position of the second and the third explanation.

Line 6, Page 6248: Can the authors provide a measurement evidence supporting "isoprene is still likely the dominant OVOC precursor"? E.g., the contribution of isoprene to the total OH reactivity of the measured VOCs.

Line 20 – 23, Page 6248: Is this because the production of HCHO and CHOCHO from isoprene oxidation is less sensitive to the change of NOx concentrations?

Line 26, Page 6248: Ozarks is not explicitly mentioned in Section 3.2.

Line 4 – 6, Page 6251: Change to "a convoluted diagnostic for assessing the VOC compositions". Because there is no evidence supporting the link between R_{GF} and ozone formation.

Line 9 – 12, Page 6251: Why should the point measurements represent the monthly mean values? OMI or GOME can provide VCDs on daily base.

Line 12, Page 6251: What does the "vertical structure" refer to?

Line 22 – 23, Page 6251: Why there could be a positive bias in CHOCHO measurements? The authors should mention this point in Section 2.1.

Line 25 – 28, Page 6251: Compared to HCHO, CHOCHO is usually produced as third or forth generation product of isoprene oxidation (c.f., MCMv3.2). Could this also cause the difference in vertical distribution between HCHO and CHOCHO?

Line 6, Page 6252: The term "column-integrated R_{GF}" is confusing. It reads like the sum up of R_{GF} over the entire vertical column. I think what the authors meant should be the R_{GF} calculated from tropospheric VCDs.

Line 20, Page 6252: Isn't it 2007 instead of 2006?

Line 2, Page 6253: "column vcds" → "vertical column densities".

Line 21, Page 6253: Please add references for "previous studies".

Line 25 – 27, Page 6253: Can you see the difference between annual averages and monthly averages from your own OMI data in 2007?

Table 3: Please describe the acronym FT in the footnote c.

Table 4: In footnote b, what about the calculation for HCHO mixing ratio?

Figure 1: I suggest to change the symbol colors of power plant well, so that the in-

dividual points can be easily seen. The same for other similar figures in the manuscript.

Figure 2: For pints below the 1% line, are they related with direct emissions of HCHO?

Figures 5, 7, and S2: Since the authors mentioned about the dependence of HCHO, CHOCHO and R_{GF} on altitude in the main text, I suggest to include the time series of flight altitude in these figures.

Figure 8d: Since the HCHO and CHOCHO measurements shown in a and b are above 200 m, the altitude range should be 200 m – 6 km instead of 0 – 6 km. The zero value of the normalized concentration at 200 m is quite confusing. What is the information the authors want to give by this plot? I could not find it in the main text.

Figure 9: I suggest to only show the region of the SENEX study, i.e., the region shown in Figure 1.

Figures S3 and S4: I suggest to add date and time to each profile number. So that it is clearer to the readers that the change of vertical structure over the time of the day.

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