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 #1

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

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, RGF 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.

While ideally 2013 OMI retrievals would be used in this analysis, the satellite has experienced severe degradation such that quantitative CHOCHO is not easily determined. Only the 2007 retrievals are available at this time. One of the major conclusions reached using the SENEX measurements is that in the SE US, R_{GF} is not a diagnostic of anthropogenic emissions, as HCHO and CHOCHO production are dominated by isoprene oxidation. Our in-situ measurements also show that R_{GF} is unaffected by NO_x and OH (section 3.3). Therefore, as long as isoprene is the dominant VOC for HCHO and CHOCHO production in the SE US in both 2007 and 2013, the comparison between 2007 satellite and 2013 in-situ R_{GF} remains valid. Both this work and analysis of the previous 1995 Nashville/Middle Tennesse Ozone Study (Le et al., 1998) find isoprene to be the dominant HCHO source. Interannual variability of summertime isoprene emissions is estimated to be between 8 and 18% for the contiguous U.S. during the summers (Tawfik et al., 2012). Therefore, it is likely that isoprene is also the dominant OVOC source in 2007.

This discussion is now included in section 3.5 (comparison with satellite retrievals).

Specific comments

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

Corrected.

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

We have now addressed this comment in section 3.5.

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 RGF been improved by these measurements?

A more careful conclusion is stated: "… [W]e conclude that satellite-based observations of R_{GF} can be used alongside knowledge of land-use as a global diagnostic of dominant hydrocarbon speciation."

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

We now use this suggested clarification.

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.

We now consistently refer to vertical column densities using the symbol Ω_V.

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

Corrected.

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

Corrected.

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.

We now include in section 2.2 that we use the average vertical column densities for June through August of 2007.

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.

We now clarify that we are referring specifically to HCHO and CHOCHO. Throughout the manuscript, we either refer to "both OVOCs" or "HCHO and CHOCHO" rather than using the more broad term "OVOCs".

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

The Ozarks are labeled in the top panel of 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.

We have reworded this to state that the concentrations of both OVOCs are higher in regions with anthropogenic influence than in the surrounding biogenically dominated areas.

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.

These cities are labeled in the top panel of Figure 1.

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?

We have reworded our explanation to state: "By comparing the observations made within 1 hour on the same day, we aim to minimize any impact diurnal variation of RGF would have on this analysis."

There are four flights for which we compare R_{GF} measured at one location to another location on the same flight. On the June 12th flight, all measurements used in the in-and-out of plume comparisons are acquired over ~1.5 hrs (Fig 7). Both in-plume and background regions are sampled multiple times, and neither show a temporal trend in R_{GF} over the time span of the observations. On both the June 10th and June 25th flights, we highlight the southeast corner of the flight track as a region of high R_{GF}. The time elapsed between measuring the observations at the southeast corner of the flight track and the northwest region of the flight track is ~1 hr. Finally, on the 26 June flight, we highlight the Ozarks as a region of low R_{GF}. The R_{GF} is low compared to the southwest portion of the flight path, which was sampled approximately 3 hours before the measurements over the Ozarks. This amount of time is considerably longer than the maximum times between measurements used in the comparisons for the other flights. For that reason, we have included it as a possible reason for the observed differences in R_{GF} in section 3.2.

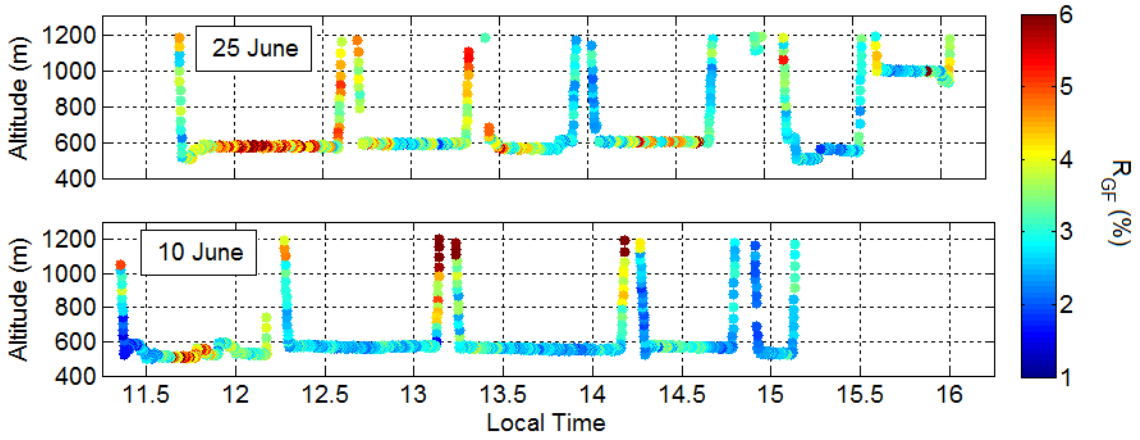
Line 26, Page 6245: "On both the 10 June and 25th flights," → "During flights on both 10 June and 25 June,".

Corrected.

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.

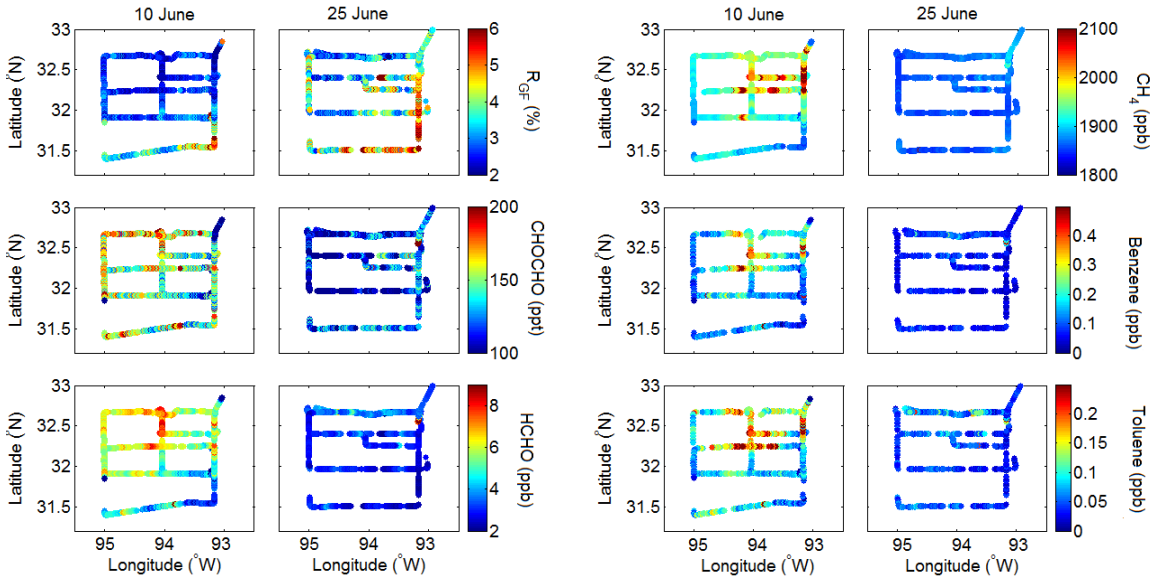
The incursion of the free tropospheric air mass appears limited to the region circled in Figure 3, as shown in Figure 5.

The figure below is a time series of altitude colored by R_{GF} for each fight. The primary flying altitude for both flights is ~600 m. The difference in R_{GF} between the two flights does not appear to be altitude driven.



While R_{GF} is typically slightly higher in the free troposphere than the boundary layer, no clear altitude dependence in R_{GF} is observed within the boundary layer (Figure 8c, altitudes less than 2 km, and figure S4 for individual profiles). Therefore, as long as measurements are acquired in the boundary layer, altitude should have little effect on R_{GF}. This is now explained further in section 3.5. Because all flight tracks remain primarily within the boundary layer, this negates the need of showing altitude measurements along the flight track.

Another possibility for the differences in R_{GF} observed on the two days is the emission strength of the underlying VOCs. As shown below, both CHOCHO and HCHO concentrations are higher on 10 June, while R_{GF} is lower. On 10 June, concentrations of anthropogenic VOCs (e.g. CH_4, benzene, and toluene) are higher. It is possible that the CHOCHO and HCHO budgets are more influenced by these AVOCs on 10 June, such that the influence of monoterpene emissions on R_{GF} is stronger on 25 June. However, this discussion is beyond the intent of our comparison, which is to compare only measurements acquired on the same flight.



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

We have eliminated the term upwind to avoid confusion.

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

Of the measured VOCs, isoprene constitutes the majority (74%) of the total OH reactivity of the measured primary VOCs for this subset of measurements. This excludes HCHO, CHOCHO, and CH_3CHO, which contribute significantly to the calculated OH reactivity. This is now mentioned in this paragraph.

Line 25, Page 6246: CO2 data is not shown in Figure 4.

For simplicity, rather than including a 5th subplot, we will not refer to CO_2 measurements. CH_4 measurements (subfigure f) fully illustrate the emissions associated with oil and natural gas production.

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.

The references that specifically discuss ozone production are now listed.

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.

Corrected.

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.

We now state that the contribution of isoprene and its first generation oxidation products methyl-vinyl-ketone (MVK) and methacrolein (MACR) to OH reactivity is more than a factor of 10 times greater than the contribution from measured AVOCs.

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?

Though the low-NO_x isoprene oxidation mechanism is still unknown, most modeling studies agree that both CHOCHO and HCHO yields are sensitive to NO_x concentrations, with lower yields at lower NO (i.e. Marais et al. 2012; Fu et al. 2008). Our results suggest that the two oxidation products are effected in a similar manner such that R_{GF} is unaffected by RO_2 fate, or that the influence of NO is counterbalanced by competing influences on R_{GF} within the plume.

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

We now explicitly state the Mark Twain National Forest is in the Missouri Ozarks.

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

We agree with the reviewer, and have changed the wording accordingly.

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

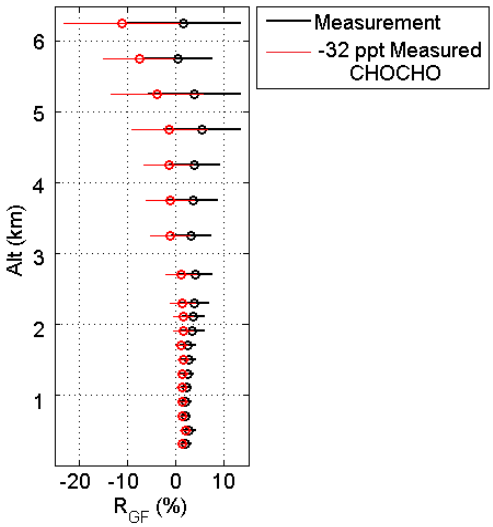
The phrase "monthly mean" is now replaced with "seasonal mean". The comparison between point and satellite values is performed on seasonally-averaged satellite data for two reasons: (1) we are reassessing the previous comparisons performed in literature, which used seasonal averages at best (though multi-year averages are also used). (2) given the error in satellite measurements, seasonal averaging is necessary to arrive at meaningful trends in regional R_{GF}.

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

We've reworded this section to explicitly refer to the vertical distribution of HCHO and CHOCHO.

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.

The potential bias we discuss is within the measurement uncertainty. The ACES instrument precision (32 ppt) is



limited by shot noise. The accuracy (6%) is limited by knowledge of Rayleigh scattering cross sections, absorption cross sections, and sample pressure and temperature. Because the uncertainty in CHOCHO concentrations from measurement precision is greater than that from measurement accuracy, we take (Measured CHOCHO – 32 ppt) as the lower limit of CHOCHO as measured by ACES. We have reworded this section to be clear that by addressing a possible bias, we are in fact addressing the measurement uncertainty, which is discussed in greater detail in Washenfelder et al. (2011). It is unclear if any bias in CHOCHO measurements exists; however, this would change the altitude dependence of R_{GF} (see figure to right).

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?

Li et al. (2014) found different mixing layer heights for the two OVOCs. They calculated that the lifetime of isoprene was shorter than the typical boundary layer mixing time, and therefore hypothesized that HCHO production happened earlier (i.e. at lower altitudes) than CHOCHO production, in agreement with the reviewer's hypothesis.

In contrast, we see that the boundary layer is typically uniformly mixed with respect to HCHO and CHOCHO, such that the two OVOCs have the same mixing height and R_{GF} is constant in the boundary later (Figure 8c, altitudes less than 2 km, and Figure S4 for individual profiles). Therefore, the time dependence of HCHO and CHOCHO production is unlikely to be the underlying cause of the difference in R_{GF} observed in the free troposphere. This can be partly explained because the profile of HCHO and CHOCHO does not only depend on production from isoprene but because the lifetimes of these two, which is longer than that of isoprene.

The second reviewer comments that heterogeneous oxidation of aerosols might release glyoxal and other OVOCs in the free troposphere (Volkamer et al., 2015), and that the heterogeneous ozonolysis of fatty acids has indeed been found to be a source of glyoxal and other compounds (Zhou et al., 2014). These discussion points are now included in section 3.5.

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.

The reviewer is correct in their interpretation of "column-integrated R_{GF}", though the term could be a source of confusion. We have reworded this section for clarity.

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

Corrected.

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

Corrected.

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

Corrected.

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

Below we show HCHO and CHOCHO vertical column densities from OMI averaged over June through August 2007 (left), and over the entire year (right). The spatial distribution of HCHO appears similar in the summer and the annual averages, likely because the high summer concentrations dominant the yearly averages. In the glyoxal averages, summertime measurements show hotspots not seen in the annual averages. This difference in spatial patterns translates to different spatial patterns in observed R_{GF} both globally and over the US.

We do not see the hypothesized lower R_{GF} in the summer compared to the annual average over isoprene dominated regions (bottom panel, ocean data not shown for clarity). However, large differences are seen in other areas, such as the boreal forests, where monoterpene emissions are high. Therefore, we keep the hypothesis that point-based measurements may be biased to display the influence of BVOC emissions on R_{GF}, but remove the example of isoprene.

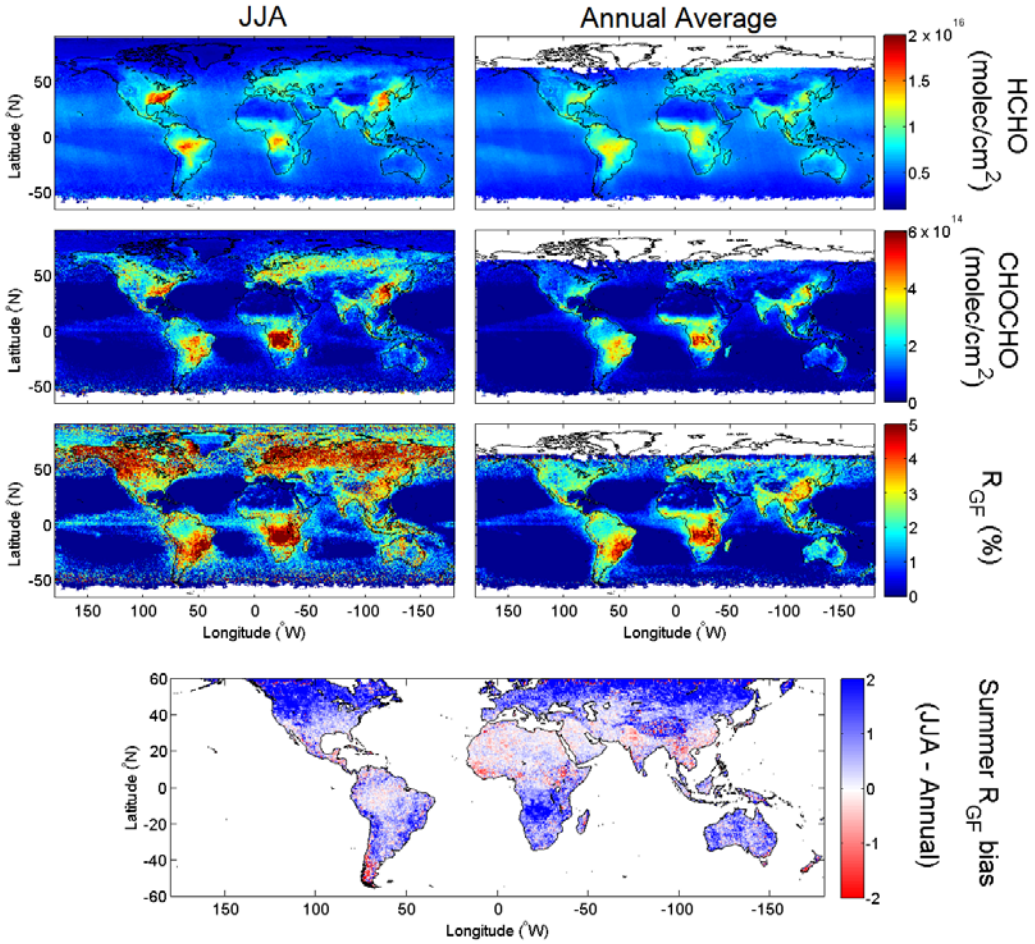


Table 3: Please describe the acronym FT in the footnote c.

F.T. (free troposphere) is now defined in the footnote.

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

We now clarify that both CHOCHO and HCHO are calculated in the same manner.

Figure 1: I suggest to change the symbol colors of power plant well, so that the individual points can be easily seen. The same for other similar figures in the manuscript.

The symbol colors have been changed.

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

These points are discussed in section 3.2 and shown in Figure 4. Direct emissions of HCHO are discussed as a potential driver for the low values of R_{GF} in this region.

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

As now discussed in section 3.5, R_{GF} is not a function of altitude within the boundary layer. Because the data shown in these figures is primarily or entirely in the boundary layer, altitude plots do not add to this analysis.

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 8d was intended to illustrate the ratio of free troposphere CHOCHO relative to boundary layer CHOCHO is greater than the same ratio for HCHO. As this information can be derived from Figure 8c, and because Figure 8d is a source of confusion, we no longer include Figure 8d in the manuscript.

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

We prefer to show the whole United States to put the measurements acquired in the SE US in context. Specifically, this map highlights that the SE US, which is dominated by isoprene, and the NW US, which is dominated by monoterpenes, have different values of R_{GF}.

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.

The day and time of the profiles are now shown in Figure S4.

References:

Fu, T. M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res., 113, D15303, 10.1029/2007JD009505, 2008.

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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.
Marais, E. A., Jacob, D. J., Kurosu, T. P., Chance, K., Murphy, J. G., Reeves, C., Mills, G., Casadio, S., Millet, D. B., Barkley, M. P., Paulot, F., and Mao, J.: Isoprene emissions in Africa inferred from OMI observations of formaldehyde columns, Atmos. Chem. Phys., 12, 6219–6235, 10.5194/acp-12-6219-2012, 2012.

Tawfik, A. B., Stöckli, R., Goldstein, A., Pressley, S., and Steiner, A. L.: Quantifying the contribution of environmental factors to isoprene flux interannual variability, Atmos. Environ., 54, 216–224, 10.1016/j.atmosenv.2012.02.018, 2012.

Washenfelder, R. A., Wagner, N. L., Dube, W. P., and Brown, S. S.: Measurement of atmospheric ozone by cavity ring-down spectroscopy, Environ. Sci. Technol., 45, 2938–2944, 10.1021/es103340u, 2011.