EGUSPHERE-2025-5285 – Author comments to RC1

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Legend: Referee comments in ***blue and italic***, author comments in **black**, changes in the manuscript text in **green**

Review #1

The paper presents a thorough multi-site analysis of the glyoxal-to-formaldehyde ratio (RGF) derived from ground-based MAX-DOAS measurements across four environments (tropical forest, temperate forest, and two urban sites). The authors attempt to clarify why the RGF values reported in different studies often diverge, emphasizing observational geometry, aerosol and NOx regimes, and temperature dependence. The topic is timely and valuable for improving the interpretation of satellite and ground-based VOC proxies.

I should note that I am not a specialist in atmospheric chemistry or VOC oxidation modeling, so my comments focus mainly on the scientific reasoning, completeness of the analysis, and clarity of interpretation. Overall, the study is carefully executed and well documented, but it still lacks several essential elements that would make the findings more conclusive. Below I summarize major and minor scientific questions and suggestions.

We would like to thank the Referee #1 for the detailed feedback, helpful comments, and advice on the manuscript. The suggestions improved the manuscript message and extended the analysis in a great way.

Detailed responses to the reviewer's comments can be found below. We hope that we have incorporated all suggestions and comments in a satisfactory way. At the end of this document, you will find a general section on additional changes we made during the review process

1. *The paper interprets RGF differences as signals of VOC source composition, yet it does not provide a quantitative link from precursor classes to CHOCHO and HCHO yields. Please add a concise mechanism-based discussion that relates RGF to isoprene, aromatics, alkenes, and oxygenates, including the role of NOx regime and OH reactivity.*

   We are working on a detailed box model study to investigate the sensitivities of R_{GF} to VOC source composition, NOx regime, and OH reactivity.

   Further, we have expanded the discussion in the RGF-NO_2 relationship section to include a mechanism-based discussion covering the influence of NOx on the VOC chemistry and OH concentrations. Furthermore, we added the link VOC precursor classes to CHOCHO and HCHO formation. Specifically, we now relate R_{GF} to differences in product yields from larger VOCs like aromatics, alkenes, smaller VOCs like methoxy. The added text draws on established chemical mechanisms summarized in Seinfeld and Pandis from 2006 (Lines 557-572).

2. *Differences in photolysis, OH loss, heterogeneous uptake, and wet removal for CHOCHO versus HCHO can alter RGF independently of emissions. Please analyze, at least qualitatively, whether the observed diurnal and seasonal patterns can be explained by lifetime contrasts. A short sensitivity test or a conceptual lifetime budget would help.*

   We added a paragraph mentioning the effects that can change R_{GF} independently of emissions in the diurnal cycle chapter (Lines 365-369). Furthermore, we added a conceptual figure in the supplement (Fig. A11) visualizing the effect different photochemical lifetimes can have on R_{GF}. The figure demonstrates that, even when neglecting other processes, differences in the effective lifetimes of CHOCHO and HCHO alone yield systematic variations in R_{GF}. This qualitative analysis supports the interpretation that lifetime contrasts may contribute to the observed diurnal and seasonal variability, although a quantitative attribution would require model-based investigation.

   Lines 365-369: Furthermore, other effects independent from emissions could have an influence, like differences in photolysis, OH loss, heterogeneous uptake, and wet removal, but our dataset does not allow to separate such effects. Resulting different photochemical lifetimes of CHOCHO and HCHO might also contribute to the shape of the diurnal cycle of R^*_{GF}. Under simplified conditions, a longer lifetime of CHOCHO compared to HCHO, results in an increase of R^*_{GF} and a decrease otherwise (see Fig. A11).

3. *The manuscript reports a robust negative dependence of RGF on temperature but does not present temperature-normalized RGF. Please include a regression-based removal of temperature effects and show the residual RGF variability that might be attributable to emission composition or chemistry. A supplemental figure would suffice.*

   We thank the reviewer for this good suggestion. We account for the temperature dependence of R_{GF} using an outlier-robust orthogonal regression approach. Data points with residuals exceeding two standard deviations are down-weighted to reduce the influence of extreme values.

   As the results were interesting, we added a subsection (3.2.2) discussing the temperature-normalised R_{GF}. The new figure (Fig. 10) shows that the seasonal variability disappears and the diurnal variability remains. Further, the response of R_{GF} due to other meteorological variables is significantly reduced after removing the temperature effect (new Fig. A2).

4. *Because photochemistry drives both CHOCHO and HCHO, actinic flux and cloudiness matter. Please document any clear-sky filtering and examine whether shortwave radiation or AOD anomalies co-vary with RGF. Summarize this in Methods and expand the Discussion with a brief correlation or stratification analysis.*

Following the comment above, we added a sentence describing the filtering methodology, and clarifying that no explicit clear-sky filtering was applied. Instead, poor viewing conditions are indirectly screened using an RMS threshold (Line 116-119).

To incorporate the additional variables, we generalized the former temperature dependence section to "Link to meteorology" (3.2), where we discuss the response of R_{GF} to dew point temperature, relative humidity, boundary layer height, short wave radiation, and wind speed (Fig. A5 and A6). However, as the variables are strongly intercorrelated the variability drops significantly after accounting for temperature effects (see response to reviewer 1 point 3).

ERA5 data does not provide cloudiness or AOD, therefore, no analysis on aerosols and clouds was performed.

5. *Opposite RGF-NO2 relationships across urban sites are described but not explained. Please provide a mechanistic discussion of how NOx modifies RO2 and HO2 pathways and shifts product yields, and reconcile the contrasting behaviors at the two city sites with local emission structure.*

We have now expanded the discussion of the R_{GF}-NO_2 relationship section (see response to point 1, reviewer 1).

Our working hypothesis is that differences in industrial sectors contributing to the NMVOC emissions lead to differences in precursor VOC composition, which, in turn, results in site-dependent yields driving the R_{GF} ratio (Lines 573-581).

6. *Quality control thresholds are described, but a quantitative error budget is missing. Please provide random and systematic uncertainties for CHOCHO and HCHO dSCDs, account for correlation between bands, and propagate to RGF. Include an uncertainty table and show how uncertainties vary by season and site.*

We added a new subsection (2.2.1) in the methodology titled "Uncertainties of R_{GF}" that draws on Pinardi et al. (2013) to discuss random and systematic uncertainties for HCHO MAX-DOAS observations. Furthermore, we now discuss systematic differences between the sites (different processing at ATTO, higher viewing elevation at Incheon, high instrument altitude at Athens).

In addition, we added an uncertainty propagation for R_{GF}, using the uncertainties from the DOAS fit. The resulting annual and seasonal uncertainties are summarized in an additional table in the supplementary material (Fig. A9).

7. *The O4 correction assumes similar vertical sensitivity for CHOCHO, HCHO, and O4. Please discuss the validity range and potential failure modes, for example under lofted layers or*

strong stratification. A short diagnostic test or a reference to AMF differences would strengthen the argument.

We refined the paragraph discussing the O4 correction extending the examples of failure modes with the strong stratification. Further we added a reference (Sinreich et al., 2013) to guide readers to a more elaborated technical discussion of the usage of O4 dSCDs for light path estimations (Lines 133-138).

8. *The paper notes that average-then-ratio versus ratio-then-average can produce different results but does not quantify the bias. Please add a numerical example using the actual time series to demonstrate the magnitude under realistic variability.*

   The bias is illustrated in Fig. 13 for both the diurnal and monthly aggregation. As the bias depends on the distribution of datapoints within each bin, it varies and it cannot be easily quantified in a generalized manner. The strongest bias we observed is around 1%pt for the 10:00 local solar time bin of the diurnal cycle in Orléans. Lines 662-669

   We added a figure in the supplement showing a time series of daily means of R_{GF} along with the instantaneous and global R_{GF} for comparison (Fig. A10).

9. *As RGF is often used in satellite validation, please include a brief comparison to coincident satellite products if available, or at least set expectations by summarizing typical satellite RGF ranges for similar environments. A limited collocation analysis or a literature-based context paragraph would be valuable.*

   As we use corrected dSCDs to compute RGF*, a direct comparison to satellite products would not be straightforward. Instead, we added a paragraph extracting R_{GF} from TROPOMI observations reported by Chen et al. (2023). The ranking of stations based on their annual means is consistent with our findings (excluding Athens as it could not be extracted due to its vicinity to the coastline). The wet-dry seasonal contrast at ATTO is also reproduced in the TROPOMI data.

   Lines 452-457: Chen et al. (2023) published global R_{GF} maps based on the TROPOMI observations for the year 2019. Although our R^*_{GF} is derived from dSCDs and therefore does not correspond to the exact same measurement volume (Sect. 3.4.1), a comparison of the magnitude of annual means is still meaningful. Extracting R_{GF} values at our measurement sites from their maps for 2019 suggests the following ranking: Incheon > ATTO > Orléans. Athens could not be identified in their maps due to its vicinity to the coastline. Furthermore, Chen et al. (2023) maps show enhanced R_{GF} values during the wet season compared to the dry season at the ATTO site, which is consistent with our observations.

10. *For the tropical site, discuss the role of biomass burning using fire counts or CO as a tracer. Show whether peaks in RGF align with burning indicators. Add a short subsection or figure in Results for seasonality at the tropical site.*

We thank the reviewer for this interesting suggestion. We agree it is a worthwhile avenue, but given the noise in our R_{GF} time series and the difficulty in robustly identifying individual events during the dry season, a rigorous analysis would require considerable effort and likely deserves a dedicated study. We therefore consider this beyond the scope of the present manuscript and leave it to future work.

11. *RGF here is derived from dSCDs that emphasize near-surface sensitivity. Please clarify how conclusions might change for VCD-based ratios or for in-situ concentrations. If possible, provide an AMF-based conversion for at least a sensitivity check.*

We examined how our results change when using VCDs derived from 30° elevation dSCDs (geometric approximation). The number of available data points drops substantially, as the higher elevation angle yields smaller columns and therefore larger relative errors, causing more data to be removed by the quality filters. Relaxing these filters increases the number of valid observations, but increases the scatter in R_{GF} lowering the interpretability.

We added two figures in the supplementary material: The diurnal (Fig. A14) and seasonal cycles (Fig. A13) using the 30° dSCD data. The variability of the CHOCHO columns is strongly reduced, whereas HCHO columns behave similarly to the figures using low viewing elevations (Fig. 5 and 6). As a result, the seasonal cycle (driven primarily by the HCHO variability) is similar, but the diurnal cycle is (driven by CHOCHO variability) becomes very noisy.

To ensure clarity, we have added explanatory text in the methodology to justify our choice of dSCDs (Lines 106–108): Measurements at 30° viewing elevation, representing a geometric approximation of the vertical column density (VCD), are shown in the supplement (Figs. A13 and A14). However, the limited number of data points remaining after filtering, together with the reduced variability of CHOCHO, renders these data unsuitable for the present analysis.

12. *Please define the representative footprint for each station under the low-elevation MAX-DOAS geometry and discuss how it affects inter-site comparability. A map and a paragraph would help readers interpret differences among sites.*

In addition to the existing Fig. 2 that shows the site environment and the viewing orientation, we added a section (2.5.5) discussing coverage and representativeness of the four sites. Further, we ran backward sensitivity simulations using the FLEXPART model to quantify the sites footprint (Fig. 4).

13. *Conclusions state that RGF is not universal. Please add two or three sentences on how chemical transport models or box models could assimilate site-specific RGF constraints to evaluate VOC mechanisms.*

Box models or chemistry transport models are well-suited for investigating how different drivers influence R_{GF}. Rather than assimilating R_{GF}, it may be more appropriate to use it as a proxy to evaluate whether a model properly captures the VOC chemistry and other influencing factors. Assimilating CHOCHO and HCHO fields directly would likely be more straightforward than assimilating their ratio.

Other changes made to the manuscript during the review process:

- Every figure changed slightly except the map.
  - Removing the prebinning changed the numbers marginally (reviewer 3 specific point 2).
  - Changed to more outlier robust linear fit for Fig. 1, changed the O4 scaling factor for O4 vis dSCD in ATTO from 0.502 to 0.519.
- Added acknowledgements
  - Added missing persons and teams for supporting the stations
- Corrected wrong end year for Orleans: Figures already included two years of data (Jul 2023 until Jul 2025), whereas the text only stated until Jul 2024.
- Inclusion of backward sensitivity runs to get a better understanding of air mass history/station footprint with FLEXPART for reviewer comments (reviewer 4, reviewer 3 specific point 11, reviewer 2 general point 2, reviewer 1 point 12). Alexandros P. Poulidis who conducted the runs is now included in the co-authors.
- Restructured some sections for clarity. Removed introductory paragraphs and descriptive sentences to reduce bloat.
- Added figure showing diurnal cycles for different seasons (Fig A1).
- Removed ATTO O_4 scaling table and the other scatter plots used to determine ATTO O_4 vis scaling factor from the Appendix.
- Move most additional figures to the supplement material. Only two figures (Fig A1 & Fig A2) should stay in the appendix.