

EGUSPHERE-2025-5285 – Author comments to RC2

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

Review #2

This study investigated the diurnal, seasonal, and weekly characteristics of glyoxal-to-formaldehyde ratio RGF over four ground-based MAX-DOAS measurement sites, with additional investigations about the dependence of elevation, temperature, and NO₂ concentrations. The study also discussed the effects of different measurement techniques in the literature of ground-based versus column-based, vertical sensitivity, temporal sampling biases, and calculation order for RGF on the differences across various reports. The analyses are comprehensive and is helpful for the generalization on the usage of RGF on the understanding of VOC emission characteristics.

We would like to thank Referee #2 for the insightful comments and questions that helped to improve our manuscript.

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

General comments

- 1. The study argued that there are various calculation methods adopted in the literature. When comparing the results in this study against prior studies, the differences are dominated by the calculation methods or the real variation of RGF temporally and spatially?*

Quantifying these effects remains challenging. Differences in the order of averaging and ratioing are expected to introduce a systematic offset, while variations in the sampled air volume imply averaging over different spatial and temporal scales, leading to differing degrees of smoothing. However, the observed discrepancies across studies are more complex than either of these factors alone can explain. In particular, the contrasting reported R_{GF} values between biogenic and anthropogenic environments, with systematically lower values reported for biogenic sources in some studies and higher values in others, cannot be attributed to offsets or smoothing effects. We therefore conclude that, while methodological differences likely contribute to inter-study variability, real spatial and temporal variation in R_{GF} should still be the dominant factor.

- 2. How spatially representative are these ground-based measurement sites?*

We added an extra section “coverage and representativeness” (2.5.5) where we discuss the spatial representativeness (see reviewer 1 point 12)

Line 305-309: The horizontal orientation of the light paths introduces an additional spatial averaging that is inherent to MAX-DOAS measurements and is illustrated in Fig 2. The retrieved dSCDs represent the concentration along the effective light path, whose length within the boundary layer depends on atmospheric visibility. Under clear conditions, photons scattered at distances of up to approximately 15 km from the instrument can contribute to the signal (Seyler et al., 2017).

3. *As the reference was taken at the high elevation angles, then naturally the analyses about the elevation effects would be close to 1 with high elevation angles. Would the uncertainties increase with elevation angles as well?*

We agree that the elevation effects should be close to 1 for high elevation angles. However, we believe that the higher inter quartile range (IQR) of R_{GF} at higher viewing elevation is due to the lower signals of both trace gases, which lead to a high variability at higher elevation, i.e. dividing small values by small values.

Having the length of the manuscript in mind (reviewer 4) and given the complexity of interpreting the elevation effects, with and without the applied O_4 correction, we decided to remove the elevation section.

4. *Why were the slant column sensitivities chosen instead of vertical column sensitivities?*

See our response to reviewer 1 point 11.

Specific comments

1. *Line 474-475: what would be the emission ratio of NO_x and VOCs over these two measurement sites? Would different emitted VOCs from different sector contribute to the different values of RGF ?*

Based on this important point raised by the reviewer, and to provide the reader with a clearer context for the sites, we computed the NO_x to NMVOC ratio and the anthropogenic-to-biogenic NMVOC ratio (AVOC/BVOC) using the CAMS - anthropogenic (CAMS-GLOB-ANT) and biogenic emissions (CAMS-GLOB-BIO) over the area indicated in the supplement (Fig. A3). For NMVOC we used the total (anthropogenic + biogenic) amount. The $NO_x/VOCs$ ratio is 0%, 26%, 50%, 66% for ATTO, Orléans, Athens, and Incheon, respectively, and the AVOCs/BVOCs ratio is 0%, 174%, 2500%, 5800% for ATTO, Orléans, Athens, and Incheon, respectively. These ratios support our site characterization. The high AVOC/BVOC ratio in Athens and Incheon reflects their strong anthropogenic influence, while ATTO is dominated by biogenic emissions. They additionally highlight the intermediate (transitional) nature of Orléans. The ratios have been added to the new Table 1.

Coming to the second part of the question: This is indeed our hypothesis to explain the different R_{GF} behaviour between the two anthropogenic sites. Assuming a consistent VOC composition per sector, regardless of the location, the higher CHOCHO emissions in Athens imply that refineries and fugitive emissions would produce more CHOCHO relative to HCHO than industrial emissions. We revised the relevant paragraphs to improve our argumentation.

Lines 573-579: Checking the top five sectors contributing to the total non-methane VOCs emissions in both cities from CAMS-GLOB-ANT (Fig. 12) shows similar contributions from solvents and road transport but differences in other sectors. Industrial processes dominate in Incheon, whereas refineries and fugitive emissions are more prominent in Athens. Assuming a consistent VOC composition per sector, regardless of the location, the higher CHOCHO emissions in Athens imply that emissions from refineries and fugitive emissions would produce more CHOCHO relative to HCHO than industrial emissions. Possible species with high CHOCHO yields include aromatics (Chan Miller et al., 2016) or acetylene/ethylene (Fu et al., 2008). However, for aromatics, Nishino et al. (2010) found that CHOCHO yield decreases with increasing NO_2 levels.

2. *Line 510-512: how would the RGF values compare between MAX-DOAS measurement sites and that coincidentally sampled from TROPOMI observations?*

See our response to reviewer 1 point 9.

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 O₄ scaling table and the other scatter plots used to determine ATTO O₄ 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.