

EGUSPHERE-2025-5285 – Author comments to RC3

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

Review #3

The article presents an observational analysis of CHOCHO, HCHO, and their ratio (RGF) across contrasting environments using MAX-DOAS measurements. The study investigates temporal variability and relationships with meteorological parameters and NO₂, aiming to improve understanding of the applicability of RGF as an indicator for VOC source attribution. It also discusses the factors contributing to discrepancies among previous studies using different methodological approaches, thereby highlighting both the potential and limitations of employing RGF as a proxy for VOC source identification. The manuscript addresses a timely, underexplored topic and is generally well-structured and informative. Before publication, several issues should be clarified or strengthened as noted below.

We thank the Referee #3 for the constructive feedback to the manuscript. The raised issues helped us to further improve the 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

Specific comments

- 1. It would be recommended that the authors further elaborate on how the substantial differences in instrument placement (10-500 m above ground) and non-overlapping measurement periods (2017-2024, varying by site) may influence the retrieved diurnal, weekly, and seasonal patterns. MAX-DOAS sensitivity to boundary-layer gases depends strongly on viewing geometry and instrument height, and differences in measurement years imply variations in meteorology and emissions among the sites.*

We added two new sections: "Uncertainties of R_{GF} " (2.2.1) and "Coverage and representativeness" (2.5.5). The instrument placement is discussed as part of the systematic uncertainties. Lines 170-173: **At Athens, the instrument is located at 500 m above sea level, while the city centre lies near sea level. Under shallow boundary layer conditions, such as in winter, the effective light path may therefore only partially sample the polluted boundary layer, resulting in lower measured columns. However, since CHOCHO and HCHO concentrations peak in summer, when the boundary layer is typically well developed, this effect is expected to be small.**

The temporal patterns are discussed in the coverage and representativeness section. Lines 301-304: **The datasets were collected during non-overlapping periods, as the station**

locations originate from long-term measurement activities. While this limits strict temporal comparability, the analysis focuses on characteristic relationships rather than direct year-to-year contrasts.

2. *MAX-DOAS data were aggregated into 30-minute bins, whereas accompanying reanalysis meteorology is hourly and subsequently interpolated. Please justify this choice. Using hourly averages for MAX-DOAS would reduce noise and ensure temporal consistency with the meteorology without interpolation.*

We thank the reviewer for the comment. The aggregation into 30-minute bins was a remaining artefact, used for merging for datasets in extended analyses that were ultimately not included in the final manuscript. Based on the discussion about averaging-ratioing order in section 3.4.4, we decided to remove the pre-binning completely. We now interpolate the instantaneous ERA5 data to the exact timestamps of the MAX-DOAS measurements (<30 minutes) (Line 190).

3. *The diurnal cycles results show higher RGF-related values in ATTO than in Orléans, which seems counterintuitive given the expected dominance of HCHO in the Amazon. Figure 4 shows unscaled ATTO values as the lowest. Could the scaling applied introduce a bias in the RGF representation at ATTO?*

The O₄ scaling is applied to correct for reduced quality in the O₄ vis retrieval in ATTO. As the detector is missing the spectral coverage of the absorption band of O₄ at 477 nm in the visible, we believe that the unrealistically high difference between the O₄ dSCDs in visible and UV (Fig. 1a) originates from the lower retrieval quality in the visible. Since the O₄ ratio has a large impact on the average R_{GF}, we decided to scale the O₄ vis dSCD to align it with the realistic behaviour of other stations. While the scaling is not perfect as it depends on the determined slopes (Figs. 1a to 1c), it prevents the misinterpretation of a systematic retrieval artefact as a real signal. As a result, the average R_{GF} value in ATTO has a larger systematic uncertainty, but the interpretation is more robust with the applied scaling.

4. *In Figure 11, it is difficult to visually confirm a systematic increase in RGF with viewing elevation. Since O4-based light-path corrections have reduced influence at higher elevation angles, applying a uniform correction across sites with substantially different instrument heights (e.g., Athens at ~500 m a.g.l.) may introduce biases. Excluding the highest elevation angles appears to yield more consistent trends, and the median pattern remains relatively stable with only a slight U-shaped variation. Please clarify how these factors may influence the interpretation of elevation-dependent RGF behavior.*

See our response to reviewer 2 general point 3. The instrument altitude of Athens is discussed in response to reviewer 3 point 1.

5. *Including relative humidity datasets in the analysis or discussion may be valuable, as it strongly influences glyoxal uptake and therefore RGF variability in different environments.*

See our response to reviewer 1 point 4.

6. *The "seasonal" analysis currently reflects monthly averages. Because hemispheric seasons differ and the sites span both hemispheres, grouping by season or consistently referring to "monthly variability" would improve clarity.*

We thank the reviewer for raising this point. We have chosen to keep the term "seasonal cycle" as it is a standard label in atmospheric sciences describing the recurring annual pattern of variability, independent of hemisphere-specific seasons. However, we made sure to indicate the different seasons for ATTO compared to the other stations (Fig. 4, 7, A2).

7. *Differences in the correlation between RGF and NO₂ at the urban sites may reflect differing emission trends, such as the recent decline in NO_x levels in Seoul (Incheon). A brief note on this possibility could enhance interpretation.*

We agree with this comment and have added a paragraph mentioning that possibility.

Lines 579-581: *There is also the possibility, that the declining NO₂ levels in Incheon (Seo et al., 2021) during the measurement period lead to a more stable R_{GF}—NO₂ relationship. But as the Incheon dataset only covers one year, the effect should be minimal.*

8. *Line 113 indicates 1–3° viewing angles, but figures include data beyond 30°. Please clarify the full range of elevation angles used in the analysis.*

Based on reviewer 2 point 3, we decided to remove the elevation dependency. All other sections use only low elevation data, except new figures for reviewer 1 point 11. These figures use dSCDs from 30° elevation angle, but are only included in the supplement.

Line 102: *In this study, we use off-axis measurements at low elevation angles from 1–3°.*

9. *Line 213: It would be helpful to include the latitude and longitude of each measurement site to clearly define their locations.*

We have added a new table (Table 1) that contains an overview over stations (including latitude and longitude) and combines multiple reviewer comments (reviewer 2 specific point 1, reviewer 4 minor point 2).

10. *Line 348: While temperature variability in ATTO is limited, a slight increase during September-October coincides with peak HCHO values; this may be worth noting.*

We have added this sentence to the relevant paragraph. Lines 423-424: *While temperature variability in ATTO is limited, a slight increase during September—October coincides with peak HCHO values.*

11. *Line 496: Please clarify the spatial representativeness of the MAX-DOAS measurements. Over what approximate horizontal extension can these observations be considered representative, and how does this compare to a point measurement assumption?*

See our response to reviewer 2 general point 2.

12. *The description of how temperature dependence was evaluated is unclear. Were data grouped into temperature bins? How does this analysis add beyond what is shown in Fig. 7 where temperature influences are already visible?*

That is correct, R_{GF} was binned to temperature intervals and then the statistics per bin have been visualized in Fig. 9. As R_{GF} showed a strong dependence on temperature, we wanted to discuss it separately. Based on reviewer 1 point 3, we extended the discussion by investigating the temperature-normalised R_{GF} (3.2.2).

13. *Figure 9 indicates a possible weekend effect in RGF. It would be helpful to assess whether the differences between weekdays and weekends are statistically significant.*

Although this relative difference of about 10% is comparable to our calculated uncertainties (2.2.1), the uncertainties are expected to affect all days uniformly and should therefore not systematically bias the reduction during the weekend.

We added section 2.4 describing the statistical approach and Table A8 in the supplementary material to show the detailed results of the test. A paragraph discussing the significance was added. Lines 472-476: *For both stations, the mean weekday R_{GF}^* exceeds the mean weekend value by 0.5 %pt., corresponding to a reduction of approximately 10 % on weekends. Although this relative difference is comparable to our systematic uncertainties, these uncertainties are expected to affect all days uniformly and should therefore not be relevant for the weekend effect. As described in Sect. 2.4, the differences between weekday and weekend are significant for Athens ($t = 4.4$, $p = 2 \cdot 10^{-5}$) and Incheon ($t = 2.7$, $p = 8 \cdot 10^{-3}$).*

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.