Reply to the comments of Reviewer#2

We sincerely thank the reviewer for the positive evaluation of our manuscript and the constructive comments. The reviewer's comments are in black, our responses in blue.

This work developed posteriori emissions of VOCs (Volatile Organic Compounds) by sectors based on the first joint inversion of TROPOMI formaldehyde and glyoxal columns using the adjoint of the MAGRITTE model. This is very important work given the high uncertainties of VOC emissions at both regional and global scales. The methodology is solid, the figures are great, and the analyses are comprehensive. I recommend authors to provide more clarifications on the chemical characteristics of the unidentified VOCs. Apart from the bias in the total VOC emissions, the speciation process is another source of uncertainty and can contribute to the bias of formaldehyde and glyoxal simulations. It would be great if this can be discussed in the paper. My detailed comments are provided as below.

Page 1, Line 10: for the unidentified VOCs, how does the model deal with this species in chemistry?

Thank you for this question. As explained in the manuscript, the photochemical oxidation of the unidentified UVOC precursors (UVOC) forms glyoxal with a molar yield of unity, resulting in a 5-day assumed lifetime. We've added the following sentence: "UVOC is assumed to react with OH at a rate constant equal to 2.315×10^{15} cm^3 $molec.^{-1}$ s^{-1}, resulting in a lifetime of 5 days for [OH] = 10^6 molec. cm^{-3}."

Page 5, Line 130-133: it's really nice to see the uncertainty analyses for the HCHO and CHOCHO retrievals from TROPOMI.

Thank you very much for your appreciation of the analysis.

Page 9, Line 266: the uptake coefficient is really high. Is it the initial uptake coefficient or the coefficient at stable?

Yes, this published value (2.9×10^{-3}) is quite high (Liggio et al., 2005). It is the reactive uptake coefficient, not the initial uptake (or accommodation) coefficient. The text has been modified to reflect this: "(...) with a uniform reactive uptake probability..."

Page 10, Sect. 3.2: in the inversion, how does it work to provide emission constraints for different glyoxal precursors? Does it keep the relative percentage (VOC profiles) unchanged, and only tune the total emissions, or the profiles are also tuned?

As seen on Equation 4, the control parameters (f vector) are defined per emission category. In other words, within each emission category (defined in Table 3), the multiplying factors ($\exp(f_j)$) are identical for all species included in the category, i.e. all species are changed in the same proportion. We added the following sentence in Sect.

3.2: "Note that the emission parameters are defined per category, i.e. the speciation within each category is unchanged by the inversion."

Page 17, Fig. 3: different revision directions for Eastern US and Eastern China based on OMI and TROPOMI. Can you elaborate more on this?

The reasons for these differences are likely related to differences in the HCHO columns between OMI and TROPOMI. Comparison of Figure 1a,b of our manuscript with Figure 6a,d of Müller et al. (2024) shows that the OMI (bias-corrected) HCHO columns are generally higher over Eastern China and Eastern US, compared to TROPOMI. We inserted the following text in the manuscript: "The reasons for these differences are likely related to differences in the HCHO columns between OMI and TROPOMI, especially at mid-latitudes. Indeed, the (bias-corrected) HCHO columns from TROPOMI (Fig. 1a,b) are generally lower than the corresponding OMI columns used by Muller et al. (2024) (their Fig. 6a,d) at mid-latitudes, and more specifically over Eastern US, Eastern China and northern Europe."

Page 19, Line 445: still curious about the chemistry of UVOC.

See above.

Page 20, Fig. 4: can you add legends in the figure? Although you have described this in the caption, it would be better to show them directly in the figure too.

Done as requested.

Page 22, Line 476: this is very useful information. The simulations over Southeast US are always off, so maybe we need both HCHO and CHOCHO constraints to revise the biogenic emissions.

As seen on Fig. 3, the biogenic emissions show a decrease after optimisation over the southeast US, when only TROPOMI HCHO is used as constraint. Fig. 6 shows essentially the same patterns, but with somewhat higher emissions.

Page 22, Line 497: Apart from the total VOCs, the speciation can play an important role in model simulations. I understand it's not quantified in the inversion, but can you explain more about the potential role of VOC speciation in your analyses, especially glyoxal inversion?

The referee is correct that the inversion results are dependent on the speciation of VOCs in the inventories. We added the following text discussing areas of uncertainty in the derivation of top-down emissions (Sect. 3.2). "The inverted emissions have uncertainties due to several factors affecting the HCHO columns, besides the magnitude of the emissions, such as the background HCHO levels due to methane oxidation, incomplete or incorrect information regarding VOC speciation in emission inventories, the VOC oxidation mechanisms, the deposition of oxidation intermediates, the transport

processes influencing the vertical profile of chemical compounds, and the NOx concentrations, known to influence the OH levels as well as the yields of HCHO and CHOCHO from key VOCs including isoprene."

Page 24, Line 521-523: the same question as #4. I'm curious how the inversion model derives the optimized emissions for glyoxal precursors.

See above.

Sect. 4.5 - Sect. 4.7 are all about the model evaluations. Can you re-organize these sections? It would be better move them from Results to a new section like "Model evaluations".

Done as requested.

References

Liggio et al., Reactive uptake of glyoxal by particulate matter, J. Geophys. Res.-Atmos., 110, 1-13, https://doi.org/10.1029/2004JD005113, 2005.

Müller, J.-F., et al., Bias correction of OMI HCHO columns based on FTIR and aircraft measurements and impact on top-down emission estimates, Atmos. Chem. Phys., 24, 2207-2237, https://doi.org/10.5194/acp-24-2207-2024, 2024.