Response to reviewer comments for manuscript: **Revising VOC emissions speciation improves global simulations of ethane and propane** by **Rowlinson et al.**

We thank the reviewers for their detailed feedback on our manuscript. We have now revised the manuscript to address the comments and provide clarification where appropriate. To guide the review process, we have copied the reviewer comments below (in black) and provided our responses (in blue).

Responses to reviewer #1:
General comments

In this study a chemical transport model was used to simulate NMVOC concentrations based on the CEDS inventory and compared to observational datasets. A particularly large discrepancy was found between the observed and simulated ethane and propane. By using regional NMVOC speciation to adjust the CEDS inventory (while keeping the aggregate NMVOC emissions the same), the simulation of ethane and propane concentrations were improved.

This paper is rightfully within the scope of ACP and should be published after minor revisions.

Authors' response: We would like to thank the reviewer for the positive and constructive comments on our manuscript. We have now revised the manuscript to address the issues highlighted by the reviewer and added further clarification where appropriate.

Specific comments

Line 70: Did you use CEDS gridded data as input to the model, or just the aggregate emissions files? The data reference citation (zenodo) is available on the CEDS GitHub site.

In both simulations we used the CEDS gridded data as input, as it is already used by default in GEOS-Chem. In the re-speciated simulation we apply a scaling factor to each NMVOC emissions in tern at the point of input to the model. This redistributes the emissions across the relevant NMVOC species. The scaling factors were calculated offline using the total and speciated NMVOC emissions from CEDS and the regional inventories. In doing so the total mass of NMVOC emission used in GEOS-Chem is maintained but redistributed across the NMVOC species. We have updated the text from line 256 to make this point clear regarding the methodology.

We have also now included the reference citation for the specific version of CEDS used in Section 2.1.

L256: "We apply the regional NMVOC speciations to the CEDS NMVOC emissions for each gridbox of the relevant regions (USA, Europe and China). This re-speciation maintains the total mass of NMVOC emissions in each grid box, but redistributes the total mass across individual VOC species according the speciation estimates in each region. This is achieved through scale factors which are applied to the emissions at the point of input to the model."

Line 116: Were measurements of hexane found in these observational datasets? In Line 81 it is mentioned that hexane was included as part of an aggregate 'higher alkanes' in the GEOS-Chem model. If not included in observational data, does this affect comparisons to the model output?

The NOAA flask data does not include hexanes. This is a good point which may partially explain the overestimate seen in the model. We have now added the following text to acknowledge this point.

L163: "The model generally underestimates higher alkanes at low concentrations, which may be in part due to the observations here including only butanes and pentanes, whereas the model aggregates a range of species including hexanes."

Line 208: To be clear, when scaling the total NMVOC in CEDS by the regional speciation, this simply disaggregates the total mass into individual species, it does not change the total mass? (I see this is specified in line 256 but may be helpful to specify earlier)

Yes, that is correct. As mentioned in the earlier answer we have now tried to make this process more clear. We have now revised the text in Section 4.0 so that it focuses on the available regional NMVOC data, and expanded the text in Section 4.1 to better clarify this point.

The conclusion section can be improved with some more discussion on potential future works that could close the gaps identified in the results. Should global inventories like CEDS make efforts to improve estimation of alkanes using regional NMVOC speciation data? Only a single model was tested in this study. Should a multi model analysis be conducted to determine whether sensitivity to alkane speciation is consistent across different models?

We thank the reviewer for this comment and agree that including these points strengthens the conclusions section. We have added the following text to the conclusions to make these points:

L393: "The improvement in simulated propane and ethane shown here indicates that global emissions inventories should take into account detailed and up-to-date VOC speciation information, including making use of regional datasets where possible. This would likely improve NMVOC simulations across various models, although differences in OH concentrations between models mean the impact of these changes may vary. In order to better understand how consistent the improvement through this methodology is, a multi-model analysis should be conducted in the future. "

Technical corrections

Figure 4 and Figure 12 axis labels have ethane specified but should be propane.
Figure 6 and Figure 14 axis labels show ethane. Is this supposed to show higher alkanes?

Yes these axes should have been labelled propane and higher alkanes, respectively. These figures have now been updated.

Line 189: "Between" is repeated.
Line 198: …it would not be sufficient "to" extend the…
Line 328: …however, "this" (incomplete sentence?)

Each of these points have been corrected in the updated version of the manuscript.

Responses to reviewer #2:
This paper presents an analysis of the impact of using different VOC speciations of emissions (i.e., relative amounts of hydrocarbons and volatile organic compounds (VOCs) for a given total amount of non-methane VOCs) in a global chemical transport model (GEOS-Chem). The majority of the analysis is evaluating the change in alkanes and aromatic hydrocarbons. The simulated mixing ratios are compared to surface observations from 2 global networks of mainly remote locations (NOAA/GML and GAW). The changes in modeled OH and ozone with the different VOC speciation of the emissions are also presented.

The topic of this paper is an important component of improving the capability to simulate tropospheric composition and air quality, as the VOC speciation of emissions inventories is a major uncertainty in atmospheric chemistry modeling. However, there are a number of deficiencies in the analysis that need to be addressed before I feel this paper would be acceptable for publication.

Authors' response: We would like to thank the reviewer for their constructive feedback and comments. We have responded to each of the concerns listed below, detailing the changes that have been made to the manuscript and their justification.

1. The lifetimes of the compounds that are used in this study need to be carefully taken into consideration in the discussion of the results.

Ethane has a lifetime of ~2 months (for OH = 1E6 molecules/cm3 and lower tropospheric temperature). This long lifetime makes it suitable to use observations even at remote sites for evaluating the emissions. However, all of the other species have much shorter lifetimes and should not be considered in the same manner. Propane and benzene have lifetimes of ~10 days, and higher alkanes, toluene and xylenes even shorter. Thus, the observations at remote sites are not really suitable for evaluating emissions of these compounds.

Thank you for these points but we have a somewhat different perspective here. The concentrations of the species measured at these remote sites is above the limit of detection and quantification, and these hydrocarbons do not have secondary sources. We exclude propene as it is believed to have an oceanic emissions source which isn't included in the model. The model's numerical precision allows us to accurately (i.e. within the numerical precision of the integrator) calculate concentrations to significantly less than the limit of detection of the instruments.

As we move away from an emission source, the error sources in the modelled concentration of the VOC will vary. Initially, as well as the error in the magnitude of the emissions, errors in the treatment of boundary layer mixing and small transport and resolution impacts will be important. As the air is transported away from emissions, larger scale meteorology and reaction with OH will become important. The longer the timescale or the shorter the lifetime the more important the errors in the reaction with OH will become. However, we don't believe that this error invalidates the assessment made here. There is still utility in comparing the model's performance with the short lived species even if it is just to highlight the increased role in the chemical (OH) uncertainty.

We believe that using the regional speciation for VOCs improves the model performance for ethane and has some benefits for propane. We don't see any improvements for other species.

2. I recommend finding observations closer to emissions source regions for the evaluation.

Many aircraft campaigns have sampled urban areas and measured the hydrocarbons presented here. An analysis of the comparison of the model results to observations from air quality campaigns would provide much stronger evidence of the deficiencies of the emissions inventories and a more reliable assessment of where they are more accurate.

We believe that the uniqueness of this paper is that it has used remote measurements for this evaluation. Previous studies have used observations closer to the source region for an evaluation (von Schneidemesser et al., 2023; Ge et al., 2024) and there are only a few usingh data from remote locations. We have updated the title of the paper to reflect this and made this point in the introduction.

New Title: "Revising VOC emissions speciation improves the simulation of global background ethane and propane."

L52-61: "von Schneidemesser et al. (2023) compared measurement ratios of NMVOCs in an urban environment with global and regional inventories, finding substantially better agreement with regional datasets, attributed to outdated NMVOC speciations in global models. Ge et al. (2024) also compared a range of NMVOC species with measurements from European sites, however there long-term observational datasets in remote, atmospheric background regions have been underutilised. The majority of modelling studies have focused on the measurements from urban environments, as these are abundant and widely used, but with atmospheric lifetimes ranging from days to several months, NMVOC compounds remain at measurable concentrations in the atmosphere even far from emissions sources.

Here we explore the causes of the model underestimate of remote ethane and propane in chemical transport models, and assess the effect of alternative regional NMVOC speciations.

3. Section 3 could be incorporated in Section 4, and Figures 2-8 removed, as their contents are included in the figures in Section 4, thus significantly reducing the length of the paper and improving readability.

Although we agree that this would reduce the length of the paper, we think it would diminish readability. The reader would have to move forward several pages in order to see the figures being described in Section 3. We also think it makes more sense to keep Section 3 independent from Section 4, as they deal with very different aspects of the paper: Section 3 summarising the base model performance and Section 4 detailing the alternative regional inventories and the application of the re-speciation method.

4. At the beginning of section 4, the discussion of MEIC speciation is very limited and does not really explain what information goes into the VOC speciation. Does it really include some local information about specific VOCs?

Yes the MEIC inventory provides speciated NMVOC emissions information for China. We have now expanded the description of this dataset to give background information on the speciation methodology.

L242: "Speciated NMVOC emissions for China in 2017 are provided by the Multi-resolution Emission Inventory for China (MEIC) (Li et al., 2017a; Zheng et al., 2018). The MEIC inventory is based on a series of models and nationwide survey data, to estimate emissions of a range of gaseous and aerosol species in China (Li et al., 2017a). The MEIC provides several speciation mechanisms for NMVOC emissions, using composite source profiles to reduce uncertainty before mapping to specific chemical mechanisms following Carter (2010). Here we use the SAPRC07 methodology which lumps species based on functional groups (Carter, 2010), as this best matches the NMVOC species that are included in CEDS and GEOS-Chem. Further details on the methodology and associated uncertainties can be found in Li et al. (2014)."

5. I find Sections 5.5 and 5.6 not very informative as they show annual averages of surface values of an apparently arbitrary collection of VOCs, and annual averages of surface amounts and zonal means for OH and ozone. This work would be far more valuable for readers if the discussion was a bit deeper, focusing on a few regions (close to sources, such as eastern U.S. and eastern China) and time periods (i.e., summer) that show significant change with the different speciations.

We agree with the reviewer that the text in the manuscript does not properly convey our intent here. The inclusion of these sections and figures was to highlight that large changes in the NMVOC emissions induce only small changes in the secondary species (OH and O3).

For the oxidants, resulting global changes of 3.8% and -0.1% for OH and O3 respectively, and maximum monthly changes of 6.8% and -2.1%, demonstrate that although the re-speciation has profound changes for key NMVOC species, the impact of this methodology is very minor for oxidants. A key part of the methodology was to maintain total NMVOC mass, but as the reactivity varies between NMVOC species, it is to be expected that there would be changes to O3 and OH. We however demonstrate that these changes are relatively minor. We therefore believe that this does not require a detailed regional or seasonal analysis, but serves to show that that model performance for ethane and propane can be improved without negatively impacting the simulation of oxidants.

Similarly, Figure 17 was not intending to show changes to arbitrary VOCs, but to show the changes to each NMVOC species which was included in the re-speciation methodology (i.e. species from Figure 9.). This method requires us to alter the emission of all NMVOC species in order to maintain the total

NMVOC emitted mass, therefore we thought it was important to show these impacts even for the species for which we don't have sufficient observational data to complete an evaluation of. The figure also demonstrates the heterogeneity of the changes, highlighting the importance of accurate speciation information in different regions.

We have now altered the text in Sections 5.5 and 5.6 to outline these issues more clearly and better emphasise the overall point.

Section 5.5 L353: "The percentage change in the global annual mean surface concentrations of the re-speciated VOCs are shown in Figure 17. As expected, almost all of the changes in surface concentrations are restricted to the Northern Hemisphere, as the scale factors are only applied to emissions in this region. Increases in ethane and propane are largest in North America and China, where surface concentrations increased by more than 200%, and the global tropospheric burdens of ethane and propane increased by 17.2% and 33.9%, respectively. Concentrations throughout the Northern Hemisphere are roughly doubled compared to the base simulation, due to the relatively long atmospheric lifetimes of ethane and propane. Other VOCs predominantly change in line with the scale factor applied in each region. Globally there is a decrease in the concentration of higher alkanes (ALK4) and aromatics (benzene, toluene and xylene), although with large regional variability. The scale of these changes is smaller than seen for ethane and propane, reflecting the smaller change to the emissions during re-speciation. Short-lived species such as ethanol, formaldehyde and propene have very localised impacts, while higher alkanes, ketones (MEK) and xylene lead to wider hemispheric impacts. Broadly the changes imposed by the re-speciation of NMVOC leads to large regional changes for each species. The species for which we have observational datasets, the impact of the emissions changes range between a small improvement (ALK4) to a substantial increase in the model bias (toluene). However given the limited observations, coupled with remaining uncertainties in the emission sources for these compounds, the loss of model skill is minor in comparison to the improvement in ethane and propane."

Section 5.6 L382: "In addition to directly influencing NMVOC concentrations, changes to NMVOC emissions can also influence atmospheric oxidation processes. Although the re-speciation of emissions maintains the total mass of NMVOC emitted, individual NMVOC species have varying reactivity (Carter, 2010) and therefore relative changes will affect oxidants such as O3 and OH. Figure 19 shows the simulated change in global mean surface concentrations of tropospheric O3 and OH, following the re-speciation of emissions. Globally the changes are very small, with changes in annual mean surface O3 and OH of 3.8% and -0.1%, respectively. The change in global tropospheric OH is similarly small (<1%), maintaining a mean annual concentration of 1.06×10^6 molec cm^{-3}. The tropospheric ozone burden increases from 313.3 Tg y^{-1} to 315.6 Tg yr^{-1}, an increase of just 0.7%. Regionally there are larger impacts, with increases in both O3 and OH of ~4-5% in East China, with a decrease of similar magnitude in OH over North America. However, despite large changes in relative concentrations of NMVOCs in the model, the changes to global atmospheric oxidation and tropospheric O3 in particular are very small."

6. An evaluation of the surface ozone could be performed with air quality monitoring data, such as that available in the TOAR database. Again, discussion in greater depth of a few regions where impacts are significant would be very helpful.

Similar to the point above, we agree that our intentions with this analysis could have been clearer. We show very small global changes to tropospheric O3 in the model, which therefore would not benefit from an in-depth analysis. The changes seen here are small compared to the variability seen in the observations and the general model bias. Although we believe we have improved the model performance for the NMVOC concentrations, this does not significantly impact the concentration of other species.

Technical corrections

While the comments above will require a significant re-writing of the manuscript, included below are some technical corrections and minor suggestions.

l. 142 (and l.300) - It is interesting that there seems to be some correlation in the bias with observation site altitude, but some reason for this difference should be suggested. With the small number of GAW sites this could just be coincidence, or have more to do with the location in relation to sources.

Significant figures: the plot legends all have integer bias values, but the text always gives the bias in 0.1% increments. Round integers seem quite sufficient and would clean up the text.

Thank you, we agree this is sufficient and more consistent with the figures. Text values have been updated to integers now.

RMSE: RMSE values are only given occasionally in the text. It would be helpful to include them in all of the plot legends. A table of all the Bias and RMSE values would also help readers.

We agree with the reviewer that this would be a useful addition. We have tried including RMSE in the figures as well as NMB, but the additional text overcrowded the figures and hindered readability. Therefore we have instead included a table (Table 1.) in section 5.5, to clearly display average values for NMB and RMSE by species and measurement type.

Table 1. Average NMB and RMSE values for each model simulation and NMVOC species.

NMVOC	Dataset	Base		Re-speciated	
		NMB (%)	RMSE (ppt)	NMB (%)	RMSE (ppt)
Ethane	GAW Measurements	-38.3	708	-8.9	430
	NOAA Flasks	-35.2	678	-3.8	489
Propane	GAW Measurements	-59.4	343	-38.6	281
	NOAA Flasks	-64.0	307	-48.0	264
Higher alkanes	GAW Measurements	81.0	492	55.9	415
	NOAA Flasks	11.2	424	-1.7	364
Benzene	GAW Measurements	-12.4	59	-25.2	61
Toluene	GAW Measurements	-27.1	61	-61.1	70
Xylene	GAW Measurements	-54.6	26	-70.0	29

Figures 4, 6, 12, 14: plot axes labels are wrong (or are the actual plots wrong?) - all labeled C2H6, but are supposed to be C3H8, etc.

We apologise for the mistake and confusion here. The axis labels on these plots have now been corrected.

Section 3.3: It would be informative to provide statistics and regression lines for only the higher alkanes points that are above the observed LOD. Indicating the LOD on the plots would be helpful, too.

The statistics and regression lines take into account only data above the LOD in the measurements, but do take into account model data below the LOD.

l. 185: systemic -> systematic

Corrected.

l. 189: The correlation is poor for toluene and xylenes most likely because of their very short lifetimes.

We have now included this point as a likely explanation for the model bias.

L185. "For benzene, the model generally performs fairly well, with a low bias of -12%, and the line of best fit showing no clear systematic bias. For toluene and xylene, there is very high variability in the comparison, resulting in larger underestimates in the model of -27% and -55% for toluene and xylene, respectively.

The larger underestimate is likely a result of their very short atmospheric lifetimes coupled with uncertainty in emissions and model OH concentrations."

l. 203: What is meant by 'large variability' in the OH rate constants for pentanes and hexanes?

It is discussed in the model description in Section 2.1 that the rate constant used for ALK4 is actually the value for butane. However ALK4 is an aggregated species which includes pentanes and hexanes, which have different rates of reaction with OH. This variability in reaction with OH is as much as double (Atkinson et al., 2006), which was the basis for describing it as having "large variability". However this was badly worded in this section, as such we have now adjusted the text to make this clearer.

L203: "The model simulation of higher alkanes (ALK4) overestimates the observations, which may be explained by the lumping of higher alkanes in GEOS-Chem. Although GEOS-Chem lumps butane, hexane and pentane into ALK4, the model then uses the OH rate constant associated with butane, which is slower than that for pentanes and hexanes \citep{atkinson}, which would cause an overestimate."

Figure 11: These plots are shown with a linear scale on the y-axis while all the others use a log-scale. The linear scale works quite well, so I wonder why log-scale was used on the others (particularly Figs. 13, 15).

Figure 11 was plotted with a linear scale while Figures 13 and 15 are on log scales for readability and clarity. While ethane concentrations varied from around 500-2000 ppt, propane and higher alkane concentrations span multiple orders of magnitude (~1-1000 ppt), making it very difficult to make out the lowest values or differentiate between the model and the observations. We also chose to have the same scale on each panel within these plots so the different sites could be related more easily. The resulting axes were what we found most comprehensible for the reader.