

# **egusphere-2023-3102: Evaluation of modelled versus observed NMVOC compounds at EMEP sites in Europe**

**Ge et al.**

## **Response to Referee #1**

We thank the reviewer for their time spent reading our manuscript and for their recommendation for publication upon addressing their comments. Below we include all the reviewer's comments and provide in blue text our point-by-point responses. Please note that all section numbers and line numbers mentioned in our responses refer to the clean revised manuscript (not the track-changed version).

### **General comments 1:**

Clarify the rationale for evaluating both 2018 and 2019, as the focus seems primarily on 2018 without clearly presenting key conclusions on the differences/similarities between years. Also, it should be important to clarify the selection of these years.

Response: One of the objectives of this study is to utilise the model in evaluating the 'goodness' of speciated emissions. To achieve this, we employed emission profiles from the UK National Atmospheric Emissions Inventory (NAEI). Our ideal scenario would involve conducting model simulations over several years to provide a better statistical basis for evaluating the robustness of our modelling results. However, this ideal is constrained in practice by the time available for this study, and the availability of speciated emission profiles, emission inventories, and ambient measurements. Firstly, hourly measurements prior to 2018 are scarce. Secondly, the latest speciated VOC emission profiles accessible from the NAEI is 2019. Thirdly, the latest sector-specific inventory provided by the Copernicus Atmosphere Monitoring Service (CAMS) is for 2018. Consequently, our model evaluation commenced in 2018, a year for which we had access to the CAMS inventory, the NAEI emission profile, and an adequate number of measurements. Regarding 2019, the modelling exhibited a performance comparable to that of 2018; therefore, to prevent unnecessary repetition, we only presented the results for 2018 in most cases.

To elucidate the differences/similarities across different years, the revised manuscript provides quantitative outcomes through Fig. 3 and 4, along with Tables 6 to 9. Additionally, the sentences in Sect. 3 (lines 315-320), Sect. 3.5 (lines 704-709), and Table 12 encapsulate a summary of these differences. Recognising that such information may have become obscured within the paper, we have taken steps to enhance clarity for our readers by adding the following lines.

#### **In Sect.2.5 lines 304-309 we added:**

“Owing to constraints in the availability of both emissions data and measurements, the analysis delineated herein mainly focuses on 2018, a year for which we had comprehensive access to the sector-specific CAMS inventory, the NAEI emission profile, and an adequate number of high-temporal-resolution (e.g., hourly) measurements. Model evaluations for 2019 and 2022 were carried out as supplementary activities, which were designed to make efficient use of both available regular monitoring and short-duration campaign measurements, providing additional evidence for robustness of our modelling results.”

#### **In Sect.4 lines 764-765 we added:**

“For most species, the model's performance across 2018 and 2019 exhibits considerable similarity when evaluated against regular, year-round monitoring measurements.”

### **General comments 2:**

(Fig. 2) What could be behind the big differences between both inventories of the total VOC emissions of “C-Other combustion” and “D-Fugitive”? Looking at the speciation used, it seems that these sectors are important for some of the species evaluated in this study.

Response: We apologise for not specifying the domain differences between the two inventories in the initial version of the manuscript. In Figure 2 of the original manuscript, the raw data from both inventories were presented according to their respective domain ranges. To clarify, Table R1 outlines the boundary coordinates for each of the two inventories, as well as for the actual model domain utilised in our study. The observed discrepancies in the sector totals for "C-Other combustion" and "D-Fugitive" between the CEIP and CAMS inventories are due to the larger domain encompassed by CEIP. This results in generally higher reported totals by CEIP for these specific sectors.

**Table R1.** Coordinates of domain boundaries

	<b>Lon-west</b>	<b>Lon-east</b>	<b>Lat-south</b>	<b>Lat-north</b>
<b>CEIP</b>	-29.95	89.95	30.05	81.95
<b>CAMS</b>	-29.95	59.95	30.02	71.97
<b>Model domain</b>	-29.95	44.95	30.05	75.95

In the revised manuscript, we recalculated the total emissions for each sector based on the precise boundaries of the actual model domain, specifically longitude (-29.95 to 44.95) and latitude (30.05 to 75.95). Following this revision, the previously noted significant differences in the "C-Other combustion" and "D-Fugitive" sectors between the CEIP and CAMS inventories have largely disappeared. The specific model domain information is added to the caption of Fig. 2 (shown below) in the revised manuscript.

As a result, we have revised the descriptions of differences between the two inventories based on the values now calculated according to the actual model domain.

**In Sect. 2.3.4 we deleted the following sentence from the paragraph in lines 217:**

“The CAMS inventory, with its smaller domain, generally reports lower sector totals than the CEIP inventory.”

**We have revised the texts in Sect. 3.5 lines 695-699 to the following:**

“For instance, the CEIP inventory identifies sector-E Solvents (24% of its total, similarly hereinafter) and sector-F Road Transport (22%) as major emitters (Fig. 2). In contrast, the CAMS inventory highlights Solvents as the most dominant sector (31%), which significantly surpasses other sectors. The second largest sector, Road Transport, which is further broken down into four sub-sectors each with their own distinct emission profiles, accounts for 15% of CAMS's annual total.”

**We have revised the texts in Sect. 3.5 lines 702-710 to the following:**

“In general, model simulations using the CAMS inventory show slightly better agreements with measurements than those using the CEIP inventory, which is likely attributable to the detailed segmentation of the Road Transport sector within the CAMS inventory. For example, using the

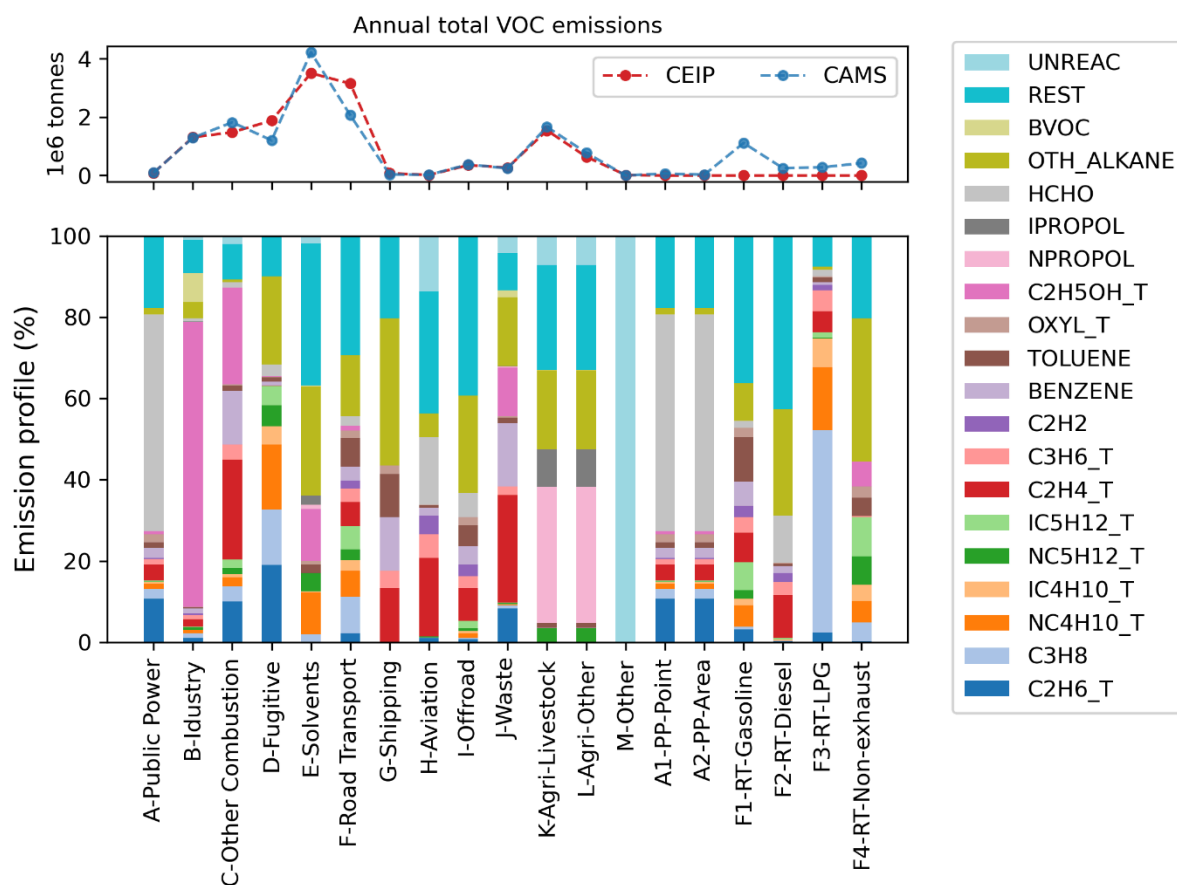
CRIv2R5Em mechanism in 2018, the mean correlation coefficient is 0.59 for CEIP and 0.64 for CAMS. Moreover, both inventories result in model overestimation of n-butane and n-pentane but underestimation of i-butane and i-pentane, which is linked to the notably low i-to-n ratios of these species emanating from the solvent sector. Such findings imply that the emission profiles have considerable influence on the agreement between modelled and measured VOC concentrations, particularly for sectors with substantial emissions. Therefore, future focus to improve model accuracy may need to shift towards a more detailed breakdown of dominant emission sectors (e.g., Solvents) and the refinement of their speciation profiles.”

**As a result, we have revised the texts in the Abstract lines 26-31 to the following:**

“Finally, model simulations employing the CAMS inventory show slightly better agreements with measurements than those using the CEIP inventory. This enhancement is likely due to the CAMS inventory's detailed segmentation of the Road Transport sector, including its associated subsector-specific emission profiles. Given this improvement, alongside the previously mentioned concerns about the model’s biased estimations of various VOC ratios, future efforts should focus on a more detailed breakdown of dominant emission sectors (e.g., Solvents) and the refinement of their speciation profiles to improve model accuracy.”

**Similarly in the Conclusions, we have revised the texts in lines 794-796 to the following:**

“Given this better model performance offered by CAMS, alongside the previously mentioned concerns about the model’s biased estimations of various VOC ratios, future efforts should focus on a more detailed breakdown of dominant emission sectors (e.g., Solvents) and the refinement of their speciation profiles to improve model accuracy.”



**Figure 2.** Annual total emissions (upper panel) from CAMS and CEIP inventories based on the same model domain (i.e., Longitude -29.95 to 44.95 and Latitude 30.05 to 75.95), and VOC profiles (lower panel) of individual EMEP sectors in CRIv2R5Em mechanism in 2018. Among the last 6 subsectors, PP stands for Public Power, RT stands for Road Transport. The speciation of sector F is an overall reflection of F1--F4. Note that CEIP does not provide data for the last six sectors (A1, A2, F1-F4), so emissions are zero for these sectors.

### **General comments 3:**

Table 4 and Fig. 3 present the same information. I would remove/move to appendix one of them.

Response: Requested change made. Figure 3 is now moved to Appendix C as Fig. C1.

### **General comments 4:**

The information provided in Section 4 feels out of place and should be introduced before. Table 5 should be moved to section 3.5 when presenting the model experiments. From L.293 to L.304, the information presented is related to the measurements and therefore should be moved to section 3.4.

Response: Requested change made. Table 5 is now moved to the end of Sect. 2.5.

**The following text related to the measurements in Sect. 4 (in the old manuscript) has been moved to Sect. 2.4 (in the revised manuscript) and now appears at lines 276-287 in the revised manuscript:**

“It is worth noting that the model-measurement comparison is complicated by the variation in the number of monitoring sites per species and in the frequency and duration of sampling time across stations. For example, the sampling duration for benzene varies from 5 to 40 minutes from DE0002R to GB0048R sites, while the model only calculates standard hourly concentrations. For this work we have matched the hourly model outputs with valid measurements at their native temporal resolution wherever we can. For instance, when using online Gas Chromatography (GC) measurements with an hourly resolution, such as CH0053R, we utilise the standard hourly model outputs. In contrast, for VOC measurements collected using the steel canister method (for example, FR0013R), these are compared with four-hour model averages (spanning 12:00 to 16:00) on the sampling day. This time frame is commonly used for canister sampling analysis, and the precise timing and duration of sampling within this time window often vary from one station to another. Therefore, due to the challenge in ascertaining these operational specifics for each station and species, we employ a model average over this period for comparison with the measured concentrations. Moreover, the annual mean concentrations discussed in this section are derived from hours with valid measurements, and where the sites have at least 65% data capture in a year.”

**The remaining text is revised to the following, lines 317-321, to provide a preamble to the whole of Sect. 3:**

“This section provides a comparative analysis between modelled and measured surface VOC concentrations for the full years 2018 and 2019, and July 2022, using measurements from the standard EMEP monitoring network (Solberg et al., 2020) and 2022 IMP. The analyses for the years 2018 and 2019 reveal similar characteristics, and the model simulations employing varied mechanisms exhibit similar results as well. To avoid repetition, figures in this section are derived from the 2018 model simulation utilising the CRIv2R5Em mechanism alongside the CAMS inventory, except where indicated otherwise.”

### **General comments 5:**

(L.293-304) It is relevant to mention the measurements' time resolution. However, I would expect that not all the stations use the same measurement techniques. This should also lead to a certain degree of uncertainty when comparing the different stations. So, it would be interesting to also mention it.

Response: We thank the reviewer for making this useful suggestion.

#### **In Sect. 2.4 lines 288-296 we added:**

“Another factor adding complexity to the comparisons between model predictions and actual measurements is the variation in measurement techniques and the inherent analytical uncertainties associated with each method. For example, of the nine valid sites providing observations of ethyne, three utilise online gas chromatography (GC) and six employ steel canisters for sample collection coupled with offline GC. The former method uses continuous online monitors which offer hourly data, while the latter uses manual grab samples in canisters which essentially provide a snapshot measurement at specific time points, typically collected two to three times per week. Moreover, even within the same measurement technique, there are discrepancies in detection limits. For instance, the online GC at site CH0053R has a reported ethyne detection limit of 4.0 pmol/mol, in contrast to the online GC at site FI0096G, which has a significantly higher detection limit of 39.0 pmol/mol. These differences further underscore the challenges in achieving good model-measurement alignment when comparing data across different stations.”

### **General comments 6:**

In section 4.2.2, when compared to other sections, I was expecting more discussion on the results. For example, some comments on the station CH0053R.

Response: We thank the reviewer for their suggestion. To provide more information on the station CH0053R, we made a new plot, Fig. 13 in the revised manuscript, that shows the time series of modelled and measured aromatic species at this site in 2018.

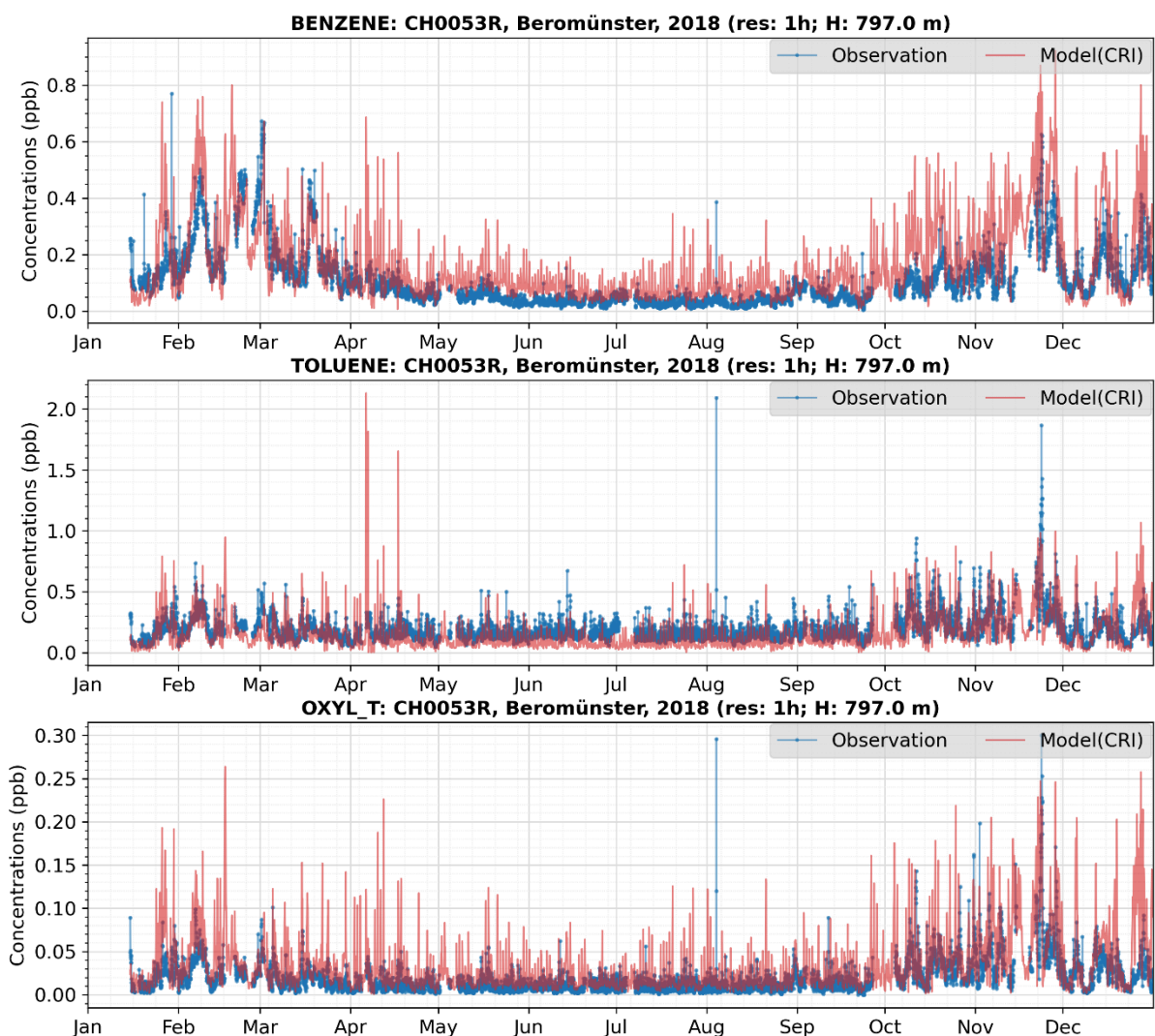
#### **In Sect. 3.2.2 lines 523-537 we added:**

“In addition, the site CH0053R might initially appear as an anomaly, particularly in the comparisons of toluene and o-xylene. However, a detailed examination of the time series for these compounds at this site does not reveal any anomalies (as illustrated in Fig. 13). For benzene, there is good agreement between model predictions and measurements, with both indicating higher concentrations during winter and lower concentrations in summer, reflecting the expected seasonal variation.

In the case of toluene, the seasonal pattern is less pronounced. The measurements indicate several spikes in concentrations reaching 2 ppb during August and November, while the model suggests multiple peaks in April. Despite these discrepancies, for most of the year, the model and measurement data align reasonably well, both showing toluene concentrations fluctuating between 0.1 and 0.5 ppb.

Regarding o-xylene, the measured concentrations are consistently low throughout most of the year, typically close to zero, leading to significant analytical uncertainties. In comparison, the model predicts generally higher concentrations of o-xylene, with numerous peaks exceeding 0.05 ppb throughout the year. This discrepancy may arise from inaccuracies in the model's input data, suggesting a potential overestimation of emission sources within the single model grid considered. Nonetheless, considering the limited data available for this compound, and its low ambient levels, both model predictions and observed values are subject to considerable uncertainties. Consequently,

there is a need for more measurements focusing on not only air concentrations but also on emissions to enhance the accuracy of these estimates.”



**Figure 13.** Time series comparisons of benzene, toluene, and o-xylene concentrations at CH0053R site in 2018.

#### General comments 7:

(L.550) The authors mention that ethyne and benzene share a similar source, but when looking at the speciation profiles (Fig.2) used for the different sectors I fail to see it. For example, the sector “C-other combustion” shows a big share for benzene but none for ethyne.

Response: This is exactly one of the key messages our paper wants to convey. The emission profile utilised in this work primarily originates from the UK National Atmospheric Emissions Inventory (NAEI), representing the most up-to-date speciated VOC inventory available to us. With these explicit emission inputs, we anticipated comparable model performance for ethyne as observed for benzene. Contrary to expectations, however, the model accurately predicts benzene levels yet struggles with ethyne. Besides, measurements (especially in winter) strongly indicate that ethyne and benzene originate from the same sources, a correlation the model fails to predict. This discrepancy underscores



that there are potentially significant flaws in the current estimates of ethyne emissions within the inventory, particularly in sectors with substantial benzene emissions, such as Other Combustion.

#### **General comments 8:**

(L.554) “...but the emission inputs need to be scrutinized and potentially revised to better reflect real-world conditions.” How so?

Response: For instance, initiating measurement campaigns to assess ethyne emission factors, specifically targeting periods of high emissions such as winter, and focusing on proximate emission sources, including gasoline vehicles, shipping, industrial and residential combustion of natural gas, waste incineration, domestic wood fireplaces, could all yield more accurate data. The new winter VOC campaign currently being planned by the EMEP Task Force on Measurement and Modelling (TFMM) presents an excellent opportunity. However, more measurements will be required for different emission activities. These targeted campaigns would likely provide valuable insights into seasonal variations and the impact of specific sources on overall emissions.

#### **In Sect. 3.2.4 lines 585-590 we added:**

“For instance, initiating measurement campaigns to assess ethyne emission factors, specifically targeting periods of high emissions such as winter, and focusing on proximate emission sources, including gasoline vehicles, shipping, industrial and residential combustion of natural gas, waste incineration, domestic wood fireplaces, and so on. More emission measurements will be required for different emission activities. These targeted campaigns would likely provide valuable insights into seasonal variations and the impact of specific sources on overall emissions.”

#### **General comments 9:**

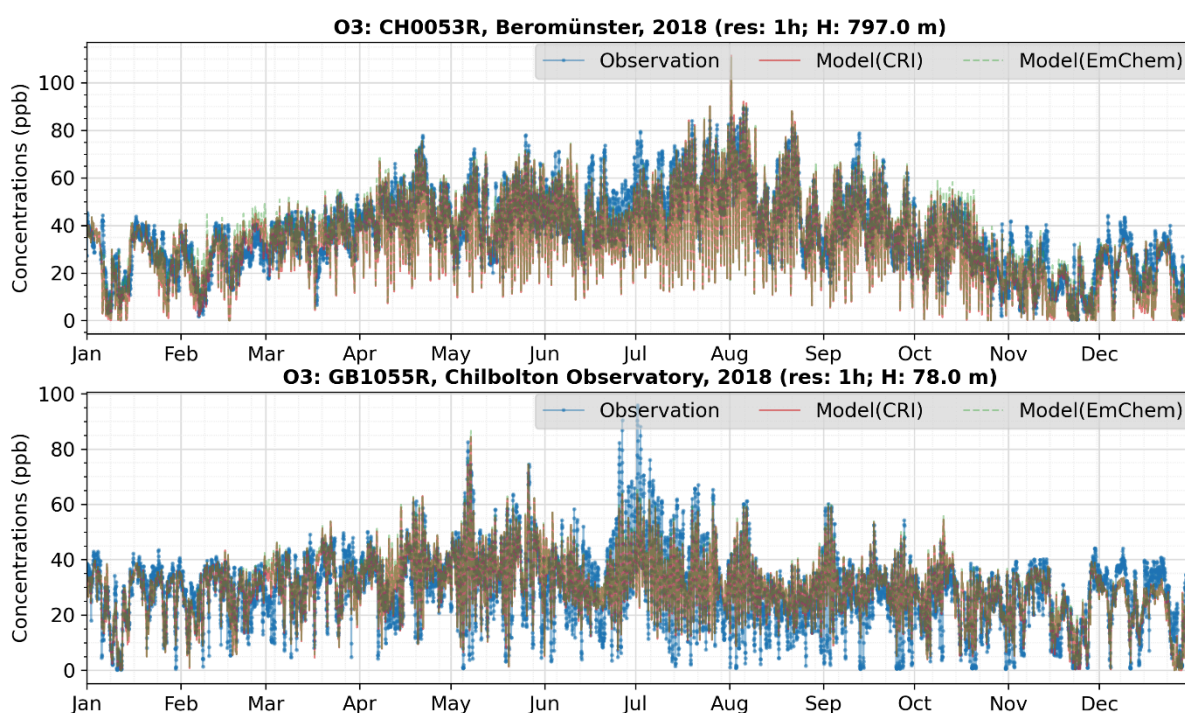
The authors mention that the default speciation in the EMEP model is EmChem19rc, so why are the results presented mainly using CRIV2R5Em (L.305)? For the sensibility analysis, could the two chemical mechanisms show a very different sensitivity on ozone to changes in VOCs?

Response: The CRIV2R5Em mechanism contains a wider array of VOC species and more detailed chemistry compared to the EmChem19rc, thus providing an illustrative example of applying CRI schemes within the EMEP MSC-W model. One of the objectives of this study is to evaluate the performance of these two schemes, and to assess how sensitive VOC comparisons are to the choice of scheme, with details presented in Sect. 2.2 lines 105-122. The findings of this research suggest that the default EmChem19rc mechanism performs comparably to, if not better than, CRIV2R5Em, for selected VOC at least.

The decision to predominantly utilise CRIV2R5Em in this study was motivated by our aim to showcase results using the most comprehensive scheme available, which, in theory, should enhance model performance. However, it's important to note that no significant difference was observed between the two schemes in terms of their agreement with the relatively sparse VOC measurement data that are currently available. It's also important to note that running simulations with CRIV2R5Em incurs substantially higher computational costs than with EmChem19rc. For example, for a given number of high-performance computing (HPC) nodes, a full year's model simulation with CRIV2R5Em requires 1.5 times the run-time needed for EmChem19rc. While this increased computational demand is manageable for research purposes, it becomes impractical for routine operational modelling, which typically involves hundreds of model runs.

In other words, this research illustrates that the default EmChem19rc scheme, despite having a smaller set of VOC species and simpler chemistry, offers the advantages of speed and satisfactory accuracy. Consequently, it emerges as a great option for most EMEP modelling applications.

Regarding the second question about ozone sensitivity, the answer is no. The VOC comparisons detailed in this study already reveal that the two mechanisms exhibit remarkably similar behaviour. Additionally, Fig. R1 illustrates that both mechanisms yield ozone concentrations that align reasonably well with the observed hourly values at two example monitoring stations, with their results nearly indistinguishable from each other. This consistency in modelled VOC and ozone concentrations suggests that the oxidation processes offered by both mechanisms are very similar. Consequently, it is anticipated that the ozone concentrations modelled by either mechanism would demonstrate similar sensitivities when subjected to variations in VOC inputs.



**Figure R1.** Time series comparisons of ozone in 2018 between measurements (blue) and model outputs using the CRIv2R5Em (red) and EmChem19rc (green) mechanisms.

#### General comments 10:

I understand that the sensibility analysis presented in section 4.6 and Appendix G is beyond the scope of the study. My main concern goes towards the selection of the speciation profile. Why did the authors use a gasoline vehicle speciation profile to represent solvent emissions?

Response: The use of the gasoline profile was pragmatic - it was technically easy to implement, and anyway provided a more reactive VOC mixture than that of solvents. In particular, the gasoline profile contains more alkene species, which could be expected to influence short-term ozone formation. It is also clear (e.g. from Oliveira et al., 2023) that solvent speciation is extremely uncertain, and it is not known which alternative speciation best fits the European situation. We have modified the text to include this extra information.



### **Technical corrections 1:**

Could be just a question of the formatting but some figures seem to appear misplaced in other subsections, e.g. Fig. 3 should be in section 3.4, Fig. 16 in section 4.3.2.

Response: We appreciate the reviewer highlighting the formatting issue. In the revised version, we have double-checked all figure placements and ensured they are in the correct subsections. For instance, Fig. 3 is now moved to the appendix as Figure C1, and Fig. 16 (now Fig. 15 in the revised manuscript) is now moved to section 3.3.2. We can note, however, it will be ACP typesetting that will decide on final placements; we can only make suggestions.

### **Technical corrections 2:**

(L.608) “ose”?

Response: We apologise for the typo here.

### **This sentence is rephrased to the following (lines 643-644):**

“The evaluation of model performance is inherently constrained by uncertainties in emissions, meteorological conditions, model parameterisation, and measurements.”

### **Technical corrections 3:**

Standardise, e.g., i-butane/iso-butane, i-pentane/iso-pentane, throughout the text.

Response: We thank the reviewer for pointing out these inconsistencies. Our intention had been to use “i” throughout our manuscript, since this terminology simplifies and standardises the expression of i-to-n ratios. However, some instances of “iso” escaped notice in the final read-through before submission. In the revised manuscript, we have checked again and corrected all “iso” to “i”.

### **Technical corrections 4:**

I leave the decision to the authors, but consider moving time series plots (Fig. 13 and 15) to the appendix.

Response: We thank the reviewer for this suggestion. Upon further consideration, we have opted to relocate the original Figure 13 to the Appendix F, where it now appears as Figure F2 in the revised manuscript. However, we have decided to maintain the original Figure 15 in its original position, where it is now labelled as Figure 14 in the revised manuscript.