Response to Referee #2

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

Detailed comments 1:
Line 10-12: I feel like the detailed configuration is not appropriate in the abstract.
Response: We thank the reviewer for their suggestion. We have now removed the specified sentences from the abstract.

Detailed comments 2:
Line 15-16: boundary conditions have the same impact for all species, why do you emphasize the impact for the latter species? Doesn’t make sense. Please elaborate more.
Response: The EMEP model specifies the boundary and initial conditions (BICs) for various compounds, including VOCs, by employing a cosine function that describes month-to-month variations and takes into account latitude effects (as detailed in Sect. 3.3.6). Consequently, the impact of BICs on the concentrations of different VOC species varies. For example, the consistent underestimation of propane concentrations by the model at all monitoring sites in both 2018 and 2019 can be partly attributed to issues with boundary conditions. This might involve an underestimation of the reference annual mean near-surface concentration, as determined from measurements at Mace Head, Ireland, or an underestimation of the seasonal cycle's amplitude, or potentially a combination of both factors. Moreover, significant spatial variations in propane concentrations at European background sites have been documented in multiple studies, as elaborated in Sect. 3.1.1, lines 332-339. This suggests that regional differences in BICs of propane may well play a role in the observed model-measurement discrepancies.

To make the description of BICs more clear to readers, in Sect. 2.3.6 lines 253-254 we added:
“Since different species have different annual means and amplitudes, the impact of BICs on the concentrations of different VOC species varies.”

Detailed comments 3:
Line 24-25: In winter, the lifetime is longer. How will the bias of meteorology and chemistry affect the model performance?
Response: In general, biases in meteorology and chemistry are likely to affect all species uniformly. During winter, the lifetimes of ethene, benzene, and ethyne should become longer to a similar extent, implying that when examining ratios such as ethene-to-ethyne and benzene-to-ethyne, changes in their lifetimes should not significantly impact the results.

As detailed in Sect. 3.2.3 and Sect. 3.2.4, the key point is the model's strong agreement with the spatial correlations and time series for ethene and benzene measurements, but not for ethyne. This discrepancy highlights potential inaccuracies in ethyne emissions, given that all three compounds are primarily emitted from combustion-related activities. Notably, while the modelled ethyne concentrations align closely with measurements during summer, they diverge significantly in winter. In contrast, modelled concentrations of ethene and benzene consistently match observations across all seasons. More importantly, measurement data reveal a strong linear correlation between benzene and ethyne during winter across all sites, suggesting they share common emission sources. However, the model fails to predict this correlation. Given that ethyne and benzene have similar atmospheric lifetimes of 6-10 days (Table D1) and originate from similar human activities, such as fuel consumption and combustion processes, one would expect them to exhibit comparable spatial and temporal variation patterns. Yet, the observed satisfactory model performance for benzene contrasts sharply with the poor performance for ethyne, particularly during winter months. This suggests that the core issue lies in the accuracy of ethyne emission estimates.

Detailed comments 4:

Line 26: It's complicated. OVOC can also be emitted from biofuel combustion, etc.

Response: We thank the reviewer for their suggestion.

To reflect the reviewer’s suggestion, we have added this info to Sect. 3.3.2 lines 633-635:

“Atmospheric sources of methylglyoxal are multiple and include direct emissions from, for example, industrial emissions, vehicle exhausts, biomass burning and biofuel combustion, and secondary formation from the oxidation of biogenic and anthropogenic precursors (e.g., isoprene, aromatics).”

We also revised this sentence in the Abstract lines 23-26 to the following:

“For OVOCs, the modelled and measured concentrations of methanal and methylglyoxal show a good agreement, despite a moderate underestimation by the model in summer. This discrepancy could be attributed to an underestimation of contributions from biogenic sources, or possibly a model overestimation of their photolytic loss in summer.”

Detailed comments 5:

Line 29-30: I don’t get the logic of this sentence. Since the performances are similar, how can you draw a conclusion on the significant impact of emission profiles?

Response: This sentence is linked to a very similar model performance that contrasts noticeably with the discrepancies between the two inventories. Following a re-evaluation of the differences in sector totals between the two inventories, as suggested by Reviewer 1, we have updated the upper panel of Figure 2 to reflect the actual model domain. Further details are provided in our response to Reviewer 1’s General Comment 2.

As a result, we have revised the text in the Abstract (lines 26-31) in line with these changes:
“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.”

**Detailed comments 6:**

Line 104: what’s the difference between these two chemical mechanisms? Why do you choose these two?

Response: The EmChem19rc is the default chemical mechanism of the EMEP MSC-W model. The CRIv2R5Em is an EMEP adaption of the Common Representative Intermediates (CRI) v2-R5 mechanism. This mechanism is the simplest variant of CRI v2, considered suitable as a reference mechanism in large-scale chemistry-transport models. The difference between the two mechanisms is that CRIv2R5Em contains a wider array of VOC species and more detailed chemistry compared to the EmChem19rc (details in Sect. 2.2 lines 104-121), thus providing an illustrative example of applying CRI schemes within the EMEP MSC-W model.

The rationale behind selecting these two mechanisms was to assess the difference in model performance when employing either scheme. The results of this study indicate that the default EmChem19rc mechanism is on a par with CRIv2R5Em. It may also be noted that we predominantly present results from CRIv2R5Em in this study. This decision is driven by our aim to highlight findings using the most elaborate scheme available, which, theoretically, should enhance model performance. Nevertheless, it is crucial to mention that no significant difference was observed between the two schemes in terms of their agreement with measurements (at least as regards the measurement data available at this time). However, running simulations with CRIv2R5Em incurs substantially higher computational costs than with EmChem19rc. 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 reasonable accuracy. Consequently, it emerges as a great option for most EMEP modelling applications.

**Detailed comments 7:**

Table 1: Don't understand to choose o-xylene as a tracer. They're active in chemical reaction, and can be produced as a secondary product. Why don't use benzene? Also, the same question for choosing C2H5OH as a tracer.

Response: In this context, the ‘tracer’ for o-xylene is coloured in green, signifying its creation for existing lumped surrogates. Benzene is explicitly simulated within the model, indicating it is processed based on its pure emissions and follows precise chemical reactions, thus eliminating the need for a tracer. Conversely, o-xylene and C2H5OH are themselves lumped surrogates within the model, which rely on aggregated emissions data. As a result, a tracer is necessary to obtain ‘pure’ concentrations that can be directly compared to ambient measurements.

**Detailed comments 8:**
Figure 4: Please improve this figure and the following ones. The labels are overlapped and hard to tell.

Response: We acknowledge the issue of label overlap and have explored various methods to present these data sets more clearly, including utilising station codes instead of full names, maintaining equal lengths for the x and y axes, and adjusting the axis aspect ratios of the plots in Python. Unfortunately, none of these approaches have successfully clarified every label for each data point. As can be observed, certain pairs of data points naturally cluster closely together, such as in the scatter plot for propane in 2018, where the differences in their modelled concentrations are very little, causing the data points to cluster near each other. Our chosen method of plotting, with equal x and y axes, provides the important benefit of positioning the one-to-one line at 45 degrees, thereby facilitating an easier assessment of the general trend regarding model overestimation or underestimation.