

egusphere-2023-3145: On the uncertainty of anthropogenic aromatic VOC emissions: model evaluation and sensitivity analysis

Referee #2

The revised version was a significant improvement. I have just one question regarding Appendix A. The additional reaction of Benzene is described as $\text{BENZENE} + \text{OH} \rightarrow \text{OH} + 0.764 \cdot \text{BENZRO}_2$. However, the reference (SAPRC99 document) provided by the author (<https://intra.engr.ucr.edu/~carter/pubs/s99doc.pdf>) on page 271 shows that the reaction is listed as: $\text{BENZENE} + \text{HO}_2 = \#0.236 \text{HO}_2 + \#0.764 \text{RO}_2\text{-R} + \#0.207 \text{GLY} + \#0.236 \text{PHEN} + \#0.764 \text{DCB1} + \#1.114 \text{XC}$. While I understand that the tracer products won't affect the main reaction, but the list of chemical reactions should be consistent with the reference.

The authors thank the reviewer for taking the time to review the new version of the manuscript.

The mechanism extension focused solely on products of interest, without altering oxidant concentrations. This simplification was chosen to avoid tracking species not accounted for in the original mechanism. Notably, $\text{TOL} + \text{OH}$ and $\text{XYL} + \text{OH}$ reactions were originally present in the CB05 mechanism, not $\text{BENZ} + \text{OH}$. TOL and XYL reactions were extended by adding only one additional product because the others were consistent with CB05. This was not the case for BENZ where the mechanism is extended with additional simplified reactions introducing only the first-generation product of BENZ oxidation to represent the partition to SOA while neglecting the rest for the sake of simplicity. The authors agree with the reviewer that the description of the reactions should be consistent with the reference or clarify any modification introduced. So in Appendix A, we have acknowledged this by adding the additional information in the legend of $\text{BENZENE} + \text{OH}$ reaction, as follows: “^a Only the first-generation product that further reacts to produce SVOC is considered from the original reference.”.

Referee #4

In general, the revised version demonstrates better structure and provides a clearer explanation for biases between modeling and observations. I recommend applying the ‘tracer’ method, to explicitly incorporate species in the MONARCH model. This would help address uncertainties that remain unresolved in the revised manuscript. For instance, it may shed light on the speculated effect of deposition velocity on biases between modeling and observation. While the authors have adequately addressed most of my comments, I provide in the following additional feedback on some of my original comments that require further attention.

The authors thank the reviewer for taking the time to review the new version of the manuscript. The answers to each specific comment can be found below in red.

We appreciate the suggestion of adopting the 'tracer' method to address the limitation of working with lumped species. While we acknowledge its potential, implementing it requires significant modifications to the MONARCH's chemical mechanism, making it infeasible for the current manuscript. While this is planned to be done in the future, we believe our approach allows us to advance in a better understanding of key aspects of VOCs representation in models related to emission uncertainties.

Lines 26-27 - The sentence should be clearer regarding the contribution of VOCs to SOA via those oxidants.

Answer: In response to a similar concern raised by another reviewer, we have further clarified the sentence as follows: “Additionally, it is important to note that human-induced atmospheric changes through land use management increase oxidant levels which can also boost natural aerosol production like biogenic SOA (Kanakidou et al., 2000)”

Response: I'm uncertain why land use management would necessarily lead to increased oxidant levels. Isn't oxidant formation primarily associated with anthropogenic activities rather than land use changes?

Answer: As highlighted by Kanakidou et al. (2000), oxidant formation is indeed primarily attributed to anthropogenic activities. When discussing changes in land use, our intention was to focus on the increase of industrial and agricultural areas, which are inherently part of anthropogenic activities. We recognize the potential for confusion and have accordingly revised the text to ensure its clarity. The revised version now reads as follows: “Additionally, it is important to note that human-induced atmospheric changes, driven by emissions from sources like industrial processes, transportation, and agriculture, increase oxidant levels, which can also enhance natural aerosol production like biogenic SOA (Kanakidou et al., 2000).”

Lines 58-70 – Not clear to me which information given here specifically refers to the UK.

Answer: To improve the readability, as also pointed out by another reviewer, we removed “in the literature” from the sentence.

Response: It is unclear whether the reasons mentioned after 'This is due to several reasons' specifically refer to the example provided for the UK or if their relevance is broader.

Answer: The authors acknowledge that the previous wording may have been misleading. To clarify that the reasons provided are general and not specific to the

example of the UK, we revised the sentence to: “This identified gap is due to several reasons:...”.

Line 249 – “Urban and suburban industrial stations were also aggregated” – what is the rationale for this aggregation?

Answer: The authors changed the sentence to include the rationale as follows: “Urban, suburban and rural industrial stations, when available, were also aggregated due to their similar observed range values and trends. This consolidation was relevant as there is only 1 urban station and 1 rural industrial station.”

Response: Given that there is only 1 urban station and 1 rural industrial station, wouldn't it be logical to mention that only suburban stations were aggregated?

Answer: As shown in Table 1, as an example, for industrial stations measuring benzene, we have 1 urban, 8 suburban, and 1 rural. So, we aggregated all station types into “industrial” as they had similar observed range values and trends. The authors acknowledged that how it was written could be misleading, so we simplified the text to: “All industrial stations were aggregated due to their similar observed range values and trends.”

Lines 312-313 – “Notably, underestimations are more pronounced during winter, suggesting a potential underestimation of road traffic cold start emissions” – For traffic? I don't see that this winter trend is significant when looking at Fig. 7 and Table 2

Answer: The authors agree that when evaluating the average of all the traffic stations, as presented in Fig.7 and Table 2, this might not be so clear to the reader. Despite this, in Table 2 we can see that the lowest MB values are in summer and the biggest in winter. This effect is more evident when looking at specific stations, e.g. stations located in Barcelona and Valencia, as presented in Figure 16.

Response: I cannot locate Figure 16. Could you please direct the reader to the table or figure where this trend can be observed? If this minor trend is only evident in a few stations, it would be advisable to restrict the discussion to those specific stations.

Answer: We apologise for the error in our previous response. We intended to refer to Figure 11, which illustrates specific stations (i.e., Barcelona, and Valencia) demonstrating that underestimations are more pronounced in winter. While we use these stations as examples, this effect is not only evident for these stations but also generalised for the majority of traffic stations. As previously mentioned, Table 2 shows the lower performance of the model for traffic stations in winter compared to spring/summer. For instance, the correlation during summer is 0.70, dropping to 0.45 in winter.

Line 363 – “chemical processes affecting VOCs” - This is not clear to me. Can you specify what kind of chemical reaction could lead to an earlier VOCs morning

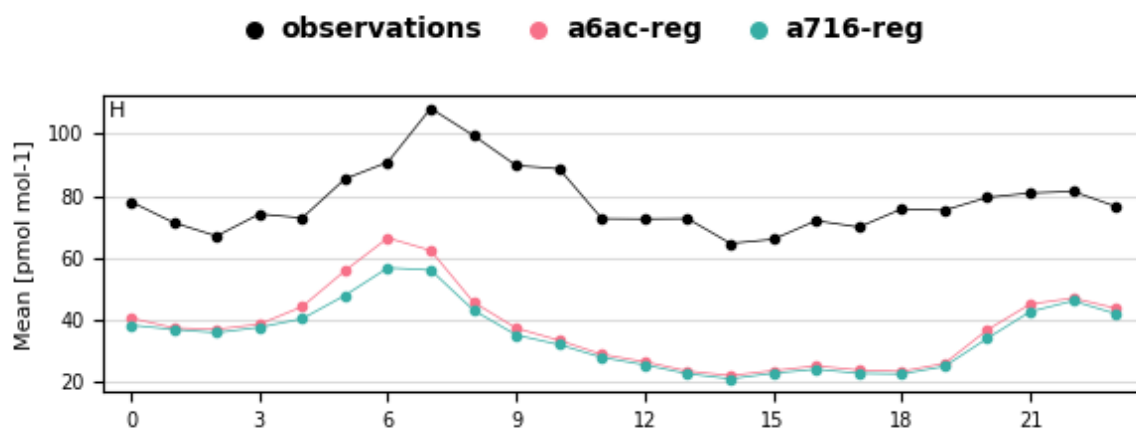
build-up compared to the measurements? Do you imply that benzene and toluene are formed by chemical reactions which occur in the morning? Could meteorological effects/stratification of the atmosphere could play a role here too?

Answer: While uncertainties in the meteorology and emissions could play a role, the authors believe that one of the main processes affecting these results is the dry deposition. This is mainly because, for the same stations, for NO₂ the model is performing well.

Response: The provided explanation is not convincing. Here, the discussion addresses the time of the peak rather than its magnitude. Different deposition values would likely affect the amplitude rather than the timing. Additionally, the agreement between simulated NO₂ and observations does not support this conclusion. Additionally, referring to 'chemical processes' in the context of dry deposition is problematic, while PBL is not a meteorological parameter."

Answer: As previously mentioned, in Figure F1, we present observed and modelled values for NO₂ for the same stations measuring VOCs. Despite the bias, the model reproduces the morning peak (around 6:00/7:00) well. This suggests that the problem related to the earlier peak observed for the VOCs may not be directly related to atmospheric effects, as it would also be observed in modelled NO₂.

We acknowledge that we are currently not fully aware of the underlying problem. Regarding our initial hypothesis, we conducted a quick test (1 week) modifying the dry deposition calculation for benzene. The scheme used in our model relies on the Henry's law constant (H^*) to scale the canopy resistance of a specific species to compute the overall deposition flux. For instance, for benzene, we adjusted the effective Henry's law constant (H^*) from 0.16 to 0.12. In the figure below, the reference run is depicted in blue and the run with modified H^* in red.



As presented in the figure, we see a slight modification of the diurnal profile rather than just changes in the amplitude. While we observe a small shift in the afternoon

peak, there are no changes in the morning peak, resulting in inconclusive findings. Therefore, further investigation and testing are necessary. To avoid misleading the reader with inconclusive results, we removed the reference to dry deposition and other initial hypotheses and replaced it with: “Further research is needed to understand the cause or combination of causes that could explain this shift.”

Line 409 – “Indicating an issue related to VOC chemistry in MONARCH’ – Can you explain why you necessarily attribute this issue to VOC chemistry? The same comment is relevant for toluene and benzene.

Answer: The authors gave a detailed explanation regarding this point in the previous comment regarding L363. To specify what we believe to be the main issue, we added in line 409 the reference to the dry deposition as follows: “...indicating a possible issue related to VOC processes in MONARCH (i.e. dry deposition).”

Response: Please refer to my response concerning the original comment on line 363.

Answer: The complete response can be found in the previous comment. This line was also changed accordingly: “At the hourly scale, the already discussed shift between observed and modelled peaks for benzene and toluene also occurs for xylene, requiring further investigation.”

Lines 612-613 – “suggesting that some sources are either not accurately represented in our model or are unaccounted for” - What about atmospheric chemistry effects and/or meteorological effects?

Answer: The authors agree with the reviewer that besides the emissions, there are several other sources of uncertainty affecting the results, e.g., the methods used in the measurements and the model performance reproducing the meteorological and chemical parameters. Therefore, this was revised in the manuscript and a paragraph was added as mentioned in the previous comment.

Response: I don't see that you addressed atmospheric chemistry and/or meteorological effects in the revised paragraph.

Answer: The authors acknowledge and apologise for the oversight that, although the topic was addressed at various instances throughout the manuscript, in the specific sentence highlighted by the reviewer, this was not introduced. Consequently, we have included this information, and the revised sentence now reads: “Despite this, it is evident that the emissions are still underestimated, suggesting that some sources are either not accurately represented in our model, are unaccounted for, or the uncertainties in atmospheric chemistry and meteorological effects are contributing factors.”.

Line 643: “this could in the model could lead to further improvements” – please revise.

The authors thank the reviewer for identifying the typo, this was revised as follows:
“Due to the different topography of Barcelona compared to Madrid, introducing this aspect into the model could lead to further improvements in its performance.”