Reply to RC1 on acp-2020-461

Taraborrelli *et al.*

December 16, 2020

Dear Anonymous Referee #1,

thank you for your thoughtful review of our manuscript. It helped us improving the manuscript considerably. Please find below a point-by-point response to your comments.

> ***Description***
> *This manuscript describes the changes in trace gas concentrations that occur when emissions of monocyclic aromatic compounds are included in a global general circulation / atmospheric chemistry model. Many recent studies have pointed out the strong influence of aromatic compounds on local and regional air quality, especially in East Asia, which makes this manuscript a timely assessment of their treatment in models and their global impacts. Here, the authors incorporate the MECCA mechanism into EMAC and diagnose the implications of aromatic chemistry by comparing a simulation with aromatic emissions turned on to one with aromatic emissions turned off. Unsurprisingly, they find that aromatic compounds contribute substantially to the global budgets of glyoxal and methylglyoxal – two of their main oxidation products and important SOA precursors – while their contributions to the budgets of smaller and more ubiquitous carbon-containing compounds, such as HCHO and CO, are smaller relative to the background. For budgets of HOx, NOx, and ozone, the effects are more complex; while aromatic emissions have small global effects (which, intriguingly, sometimes contradict those found by previous studies), their local effects can be moderately substantial and can vary in sign depending on local chemistry.*

Reply:
We appreciate Referee #1 for the accurate and synthetic summary of our manuscript.

> ***General comments***
> *The manuscript is straightforwardly written, well laid-out, and presents its findings clearly. Furthermore, because the authors use a highly comprehensive mechanism based on MCM, the chemical outcomes of aromatic oxidation are likely more robust than previous studies. However, it appears from looking more closely at the mechanism that some of the larger aromatic species (e.g. xylene and ethylbenzene) are not actually treated explicitly, but are oxidized in pathways identical to those of toluene with a "LCARBON" counter species denoting the carbon imbalance that arises from this treatment. This should be more explicitly described in the manuscript, which appears to imply that all aromatic species are treated independently by providing their individual emissions.*

Reply:
Indeed we have not made this aspect clear. In the model description (Section 2) we now stress this approximation and the error it may result from for prediction of stable products and low volatile compounds contributing to SOA formation.

> *Another general concern is that in many places model outcomes are simply described without sufficient discussion of their causal pathways, which strongly diminishes the usefulness*

> *of these findings. Further, many of the important effects of these model outcomes are only touched on without any quantitative discussion – e.g., the changes to methane lifetime and SOA formation from glyoxal and methylglyoxal.*

Reply:
We have put significant efforts in discussing the results but we are happy to improve the manuscript in this respect by following specific indications. Concerning the first specific effect that Referee #1 pointed to, we acknowledge that the quantification of the impact on methane lifetime could have been given more space than a short mention without referring to Table 4. Therefore, we have extended the paragraph L129-132 by pointing explicitly to Table 4 and shortly discussing the changes in OH and CH4 lifetime in the two hemispheres. With respect to the second specific effect Referee #1 pointed to, SOA formation from α-dicarbonyls, we think this is beyond the scope of the present manuscript for the following reason. The simulations were performed with a VBS-based approach to model condensation of organic vapours, at the time of writing of the manuscript no representation of oligomer formation from (methyl)glyoxal was implemented in the EMAC model yet. This is now implemented explicitly for cloud droplets (Rosanka et al., 2020) and its effect is planned to be assessed in a subsequent study together with the contribution of reactive uptake of epoxides from isoprene and aromatics. We have extended paragraph L201-209 by adding this explanation.

> *Specific instances are pointed out in the comments below. Finally, while the short discussion of uncertainties in Section 4 is a particularly useful addition to this manuscript, it does not go far enough to provide the reader with either quantitative or qualitative bounds on the model outcomes described herein. Of particular note, more attention should be paid to:*
> *(a) the effects of grid resolution – given that there's a lot of spatial heterogeneity in model outcomes, and the effects even change sign depending on local conditions, is 1.875 square enough to resolve this chemistry? What outcomes might be masked by the artificial mixing that occurs in such large-scale grid boxes?*

Reply:
We thank the reviewer for pointing to this important aspect that, indeed, we have not mentioned in our manuscript. We gladly take this chance to discuss the influence of (horizontal) spatial resolution on the predicted changes of trace gas levels. We now shortly mention it in our extension of paragraph L129-132 concerning OH and methane lifetime . Moreover, we add a whole paragraph in Section 4 on model uncertainties in which we frame and formulate our expectation for modelled HO_x, NO_x and O_3.

> *(b) uncertainties in chemical mechanisms, especially the newly implemented ones described in the bullet point list in Section 2 –while there is some discussion in Section 4 of the uncertainty in the phenoxy + O3 reaction, it should be put into a larger context and more explicitly tied to the uncertainty bounds of model outcomes that might be expected given the uncertainties in the chemical mechanism;*

Reply:
We agree with Referee #1. We have expanded Section 4 by discussing the uncertainties associated with the limitations of currently accepted oxidation mechanisms like the MCM. Specifically, we now mention the uncertainty on the epoxide formation pathway that is treated as direct in the MCM. This likely involves intermediate steps implying an epoxide yield dependent on NO_x and HO_x levels (Vereecken, 2019).

> *and lastly (c) uncertainties in emissions – while these are also discussed briefly in Section 4, the scope of the discussion is very limited and does not leave readers with any quantitative understanding of how well the emission totals are known, what their overall inter-annual variability might be, and how this could affect the model outcomes described*

in Section 3. I am not trying to argue that the authors need to perform additional sensitivity simulations, but the uncertainties merit a more lengthy,detailed, and quantitative description than is provided here.

Reply:
We agree with Referee #1 and therefore we expanded paragraph L243-247 of Section 4 by discussing magnitude and inter-annual variability of aromatics emissions from biomass burning, anthropogenic activities and terrestrial vegetation.

Specific Comments
Additional (more specific)questions about uncertainty are given below.
L 19 - Does the 200-300 Tg/yr refer to Tg O3?

Reply:
Yes, it does. We believe that in the relative sentence it is clear that we refer to O_3.

L 69-72 - Because the primary findings of this paper rely so heavily on the magnitude of these emissions, some small discussion of their uncertainty is warranted. Do the sources from which the inventories were derived describe the range of plausible emission amounts? Do different anthropogenic or biomass burning inventories give different emission amounts? EDIT - I see this is partially addressed in Section 4 (though it would be useful here to direct the reader to the later discussion of uncertainties). However,the short paragraph about emissions uncertainties still lacks quantitative detail, and most of the questions above still remain unanswered. Also, can a numerical range of inter-annual variability of total pyrogenic aromatic emissions be provided?

Reply:
Referee #2 made a similar point in the general comment above. We agree and have expanded the relative paragraph in Section 4 and mentioned in our reply above.

L 75 - It would be helpful here to give detail not only on the additions that have been to the mechanism, but also on generally what simplifications were made to MCM to arrive at MECCA. I realize that's available in Cabrera-Perez et al. 2016, but the reader should be able to get a sense of the methodology here without having to fully read another paper. In particular, it is problematic that this manuscript implies a full detailed mechanism for the suite of aromatics shown in Table 1 when in fact many of them just use the same oxidation schemes.

Reply:
We thank Referee #1 for making us aware of this aspect. For that we have added a short description of the simplifications made to the MCM mechanism for benzene and toluene. This is now combined with the mentioning of the LCARBON species counter as requested in your general comment.

L 122-124 - This is not a complete explanation of the OH increase in high-NOx regions. It is stated that the increased OH is "caused by the reaction of NO with HO2", but it was also stated two lines previously that NO decreases in these regions. Does HO2 increase enough as to offset both the NO decrease and the OH decrease through direct reaction with aromatics? What causes such a pronounced HO2 increase? Further,Figures 4 and 5 are not particularly useful to the reader without an explanation of why these effects occur. What causes the seasonal variability in the effects of aromatics on OH? Why are they strongest in the upper troposphere?

Reply:
The increase in HO_2 indeed overcompensates for the decrease in NO resulting in enhanced OH levels

over regions where radical production is not NO_x-limited. The HO_2 production from VOC oxidation is a well established knowledge in atmospheric chemistry. In *AROM* compared to *onlyMCM* this production is further enhanced by the photolysis of ortho-nitrophenols and benzaldehyde that we have mentioned in the manuscript. We have modified the manuscript in order to make this point clear.
With respect to Figure 4 we have added a brief explanation of why the largest decrease in planetary boundary OH is computed for the NH.
With respect to Figure 5 we have added an explanation for the reduced OH levels in the upper troposphere. The predicted changes are associated to similar reductions in NO_x. In fact, the upper troposphere is in general NO_x-limited and the oxidation of aromatics enhances the formation N_2O_5 and HNO_3 which are lost heterogeneously. This leads to an effective removal of NO_x from the gas phase and lowers the radical production.

> *L 123 - Is this "positive correlation" a quantitative effect, diagnosed by some sort of regression analysis (across time? or just regions?), and if so, can it be explained in more detail here? If this "positive correlation" is just meant to say that including anthropogenic emissions causes an increase in OH, then this phrasing is misleading – better just to state simply that OH is higher in AROM than NOAROM in these regions. Also,are these correlations really diagnosed from anthropogenic emissions in particular, or from the inclusion of all aromatic emissions (including biogenic and pyrogenic)?*

Reply:
We apologize for this misleading formulation. We have modified the sentence as suggested by the Referee by removing the use of the word "correlation".

> *L 132 - The increased methane lifetime is likely to be of great interest to readers. Can it be quantified?*

Reply:
It is quantified and also broken down for the two hemispheres in Table 4. As mentioned in the reply to the general comments above, we expanded paragraph L129-132 in which we have made an explicit reference to Table 4 and quantify the change in calculated methane lifetime.

> *L 138-140 - The same comment above (L 123) applies here to the "correlation" phrasing.*

Reply:
We apologize again for the misleading formulation and have changed the text similarly as mentioned in the answer above.

> *L 141 - It appears Figure 9 is discussed here in the text before Figures 7 (L 143) and 8 (L157)*

Reply:
Thank you for pointing to this. We fixed it in the revised manuscript.

> *L 141-145 - The same comment above (L 122-124) applies here; why do these seasonal and zonal patterns arise?*

Reply:
The inter-hemispheric changes in O_3 are indeed similar, although much less pronounced, and not independent from the changes in OH. In the revised manuscript we describe it and stress more the connection to changes in OH.

> *L 153 - Can some more quantitative description of the variation with tropopause definition (and a description of the definition itself) be included here? What specifically is meant by "robust"? Figure 7 makes it look instead like there are large absolute differences right at the tropopause, which would imply that the definition might be highly important.*

Reply:
We have extended the caption of Table 4 by listing all 6 different definitions and diagnostic "tropopauses" that are calculated by EMAC with the MESSy submodel TROPOP (Jöckel et al., 2010). In the caption we also report that the results do not change by more than 0.05 %.

> *L 154 - What is meant by "these changes", and why does the explanation provided here differ from those above (L 134-136)?*

Reply:
We acknowledge the inconsistency and the lack of clarity of this formulation. What we wanted to highlight is the direct ozone loss by reaction with (substituted) phenoxy radicals that we find to play as an **additional** and previously overlooked ozone sink at global scale. We have now reformulated the corresponding sentence in this sense.

> *L 159 - Extra close-parentheses.*

Reply:
Corrected.

> *L 143-164 - This paragraph is long and covers a wide range of different topics; consider splitting it up? Also, the sentences around L 156-160 seem to be in an odd order; the sentence beginning "However, with aromatics" seems like it should be followed by the sentence beginning "Ozone is known to react", while the two intervening sentences seem like a non sequitur.*

Reply:
We thank the Referee #1 for this comment. We now split the long paragraph where we start discussing the direct losses of ozone in the oxidation of organic compounds. Our sentence beginning with "However, with aromatics" is meant to stress that all the other global atmospheric chemistry models do not represent additional direct loss of ozone in VOC oxidation. We hope that our explanation clarifies the issue.

> *L 161-164 - How well is this chemistry known? The cited study describes the reactions of the phenoxy radical with O3 and with other phenoxy radicals, but presumably this is also in competition with many other reactions, including possible unimolecular re-arrangements or decomposition. Have competitive studies been reported? If not, can some estimate of competing reactions rates be used along with the uncertainty bounds of the phenoxy + ozone reaction rate to determine some level of certainty for this discussion here? Considering how strong the simulated effect is, and how its catalytic nature under some conditions could magnify even small errors, some discussion of uncertainty is warranted. EDIT - I see this is partially addressed below in section 4 (it'd be nice to have some parenthetical here directing the reader to the later discussion on uncertainties). Some questions remain, though – most notably why the rate constant"has to be regarded as a lower limit" (L 227) and whether competing reactions might also be uncertain.*

Reply:
We thank the Referee #1 for this useful comment. The chemistry of phenoxy radicals is indeed not very well known. The rate constant for the reaction with ozone has been determined at only ambient temperature. The latter is a lower limit because of the nature of the kinetic experiments and analysis

conducted by Tao and Li (1999). Phenoxy radical is very stable radical and the only other known sink is the reaction with NO_2, which yields ortho-nitrophenols. The rate constant of the latter reaction is about one order of magnitude higher. However, ozone is very often more abundant than NO_2 by more than an order of magnitude. This makes ozone to our knowledge the major atmospheric sink for phenoxy radicals. The reaction with NO is reversible and not considered neither in MCM nor in our mechanism. We have mention these additional sinks for phenoxy in the manuscript. However, we did not mention the relative magnitude of the rate constants and neither did we make a statement about ozone being the major atmospheric sink of phenoxy radicals. We now mention this aspect in the revised manuscript and have added a reference to the discussion of the mechanistic uncertainties in Section 4.

> *L 164 - No period (assuming this is the end of the sentence).*

Reply:
Yes, we now close the sentence with a column.

> *L 173-174 - How does nitrophenol photolysis come into play here for the phenoxy radicals? R1 implies either that nitrophenol photolysis does not form phenoxy radicals or that the mechanism skips the phenoxy radical step and goes directly to decomposition products.*

Reply:
The HONO-channel in the photolysis of ortho-nitrophenols is predicted to form phenyloxy radicals which likely rearrange to a 7-membered ring radical and further decomposes (Vereecken et al., 2016). Formation of phenoxy radicals from photolysis of ortho-nitrophenols is not skipped. However, we acknowledge that the OH-channel, which may be much more important of the HONO-channel, produce nitrosophenoxy radicals might efficiently react with ozone similarly as phenoxy radicals. However, this chemistry is unknown. In Section 3.2 we now refer to Section 4 where we already discuss these mechanistic uncertainties.

> *L 186-187 - This phrasing does not make it particularly clear which simulation has the higher NO3 concentrations.*

Reply:
Indeed it is not clear. We have modified the first part of the sentence by starting with "Relative to *NOAROM*, in *AROM* ..."

> *L 188 - Why does this effect occur in places with pyrogenic aromatic emissions, while the HOx and O3 effects described previously are more strongly associated with anthropogenic emissions? The same question applies to the HONO increase on L 191.*

Reply:
We are not sure why these decreases are predicted and suppose is a result of complex interplay of factors. Thus, we refrain to make statements not backed by a solid understanding. We added to the manuscript that these changes are modest and stress more the widespread increase of NO_3 levels by the reaction of phenyl peroxy radicals with NO_2.

> *L 198-200 - What is the explanation for these findings?*

Reply:
We think this is due to the concurrent enhancement of OH levels which "curb" the enhancement of HCHO in China, Europe and US. We have modified the text in order to express this explanation.

> *L 208-209 - Was the effect on the SOA budget quantified here? It seems this effect would be of great interest to some readers.*

Reply:
No, it was not quantified in this study. However, it will be subject of future studies in which the production of oligomers from dicarbonyls in the condensed phase is represented. Recently, we have added the cloud processing of dicarbonyls to the scavenging module of MESSy (Rosanka et al., 2020) and will evaluate the impact of it on the SOA budget in a future study.

> *L 218 - It seems odd that so much detail is shown in the many other figures for other species discussed in this manuscript, but this interesting finding for CO is not shown.Can a CO figure be added, and can an explanation be given for these spatial effects?*

Reply:
We understand Referee #1 but we had the feeling we had already too many figures in the manuscript. We are happy to add to the manuscript the figure showing the zonal mean differences for CO which peak in the NH UTLS.

> *L 230-231 - It was earlier implied (L 173-174) that the model *does* account for the effects of photolysis of nitrophenols. Can this be clarified?*

Reply:
The model accounts for the known photolysis of ortho-nitrophenols yielding HONO. However, our model does not account for the less known OH-channel potentially yielding nitrosophenoxy radicals (Vereecken et al., 2016), which might react similarly as phenoxy radicals. At the time of finalizing the chemical mechanism we were not aware of the results by Vereecken et al. (2016). Nevertheless, we state clearly in Section 4 that our model lacks photolysis of nitrophenols yielding phenoxy radicals. In this section we have replaced "reforming phenoxy radicals" with "forming nitrosophenoxy radicals".

> ***Technical comments***
> *Table 5 is cut off by the end of the page.*

Reply:
We apologize for this inconvenient. The table is not cut off in the ACP article layout. We report the complete table here at the end of the document (see Table 1).

> *Can the OH mixing ratios in Figures 3-5 be expressed instead in the more commonly used concentration units?*

Reply:
We know that OH abundance in the atmosphere is usually expressed in moleccm^{-3}. However, doing it in our manuscript would introduce an exception and an inconsistency to the way we present the results. For this reason we would like not to modify the units.

> *Figure 4 is very confusing. What are the units on the left plot? Why are there two very close blue and red lines in the left plot? Why does the caption reference solid and dashed lines in the right plot when only solid lines exist? The same questions apply to Figure 9.*

Reply:
In all Figures of this manuscript, the plotted values correspond to the original output values in mol/mol multiplied by ten to a certain power. For example, the values on the vertical axis of Fig. 4 (left) stand for mol/mol multiplied by 1e+14. Since this notation is not intuitive, we changed the titles of the plots and added the unit (e.g. "x 10^{-11} mol/mol").
The caption is indeed not clear, as the dashed and solid lines are only in the left plot of Fig. 4 and Fig. 9 (they distinguish the results of AROM and NOAROM). We changed the caption of Fig. 4 to: "Left: Seasonal cycles of OH daily (24 h) mixing ratio means (in 10^{-14} mol/mol) in the planetary

boundary layer (PBL) for AROM (solid line) and NOAROM (dashed line). Right: Relative difference (expressed in %) between AROM and NOAROM. In blue, values for the NH; in red, values for the SH...." We changed the caption of Fig. 9 to: "Same as in Fig. 4 for ozone (the unit in the left plot is 10^{-8} mol/mol).

References

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), Geosci. Model Dev., 3, 717–752, https://doi.org/10.5194/GMD-3-717-2010, 2010.

Rosanka, S., Sander, R., Wahner, A., and Taraborrelli, D.: Oxidation of low-molecular weight organic compounds in cloud droplets: development of the JAMOC chemical mechanism in CAABA/MECCA (version 4.5.0gmdd), Geoscientific Model Development Discussions, 2020, 1–18, https://doi.org/10.5194/gmd-2020-337, URL `https://gmd.copernicus.org/preprints/gmd-2020-337/`, 2020.

Tao, Z. and Li, Z.: A kinetics study on reactions of C_6H_5O with C_6H_5O and O_3 at 298 K, Int. J. Chem. Kinet., 31, 65–72, https://doi.org/10.1002/(SICI)1097-4601(1999)31:1⟨65::AID-KIN8⟩3.0.CO;2-J, 1999.

Vereecken, L.: Reaction Mechanisms for the Atmospheric Oxidation of Monocyclic Aromatic Compounds, chap. Chapter 6, pp. 377–527, World Scientific Publishing, https://doi.org/10.1142/9789813271838_0006, URL `https://www.worldscientific.com/doi/abs/10.1142/9789813271838_0006`, 2019.

Vereecken, L., Chakravarty, H. K., Bohn, B., and Lelieveld, J.: Theoretical study on the formation of H- and O-atoms, HONO, OH, NO, and NO_2 from the lowest lying singlet and triplet states in ortho-nitrophenol photolysis, Int. J. Chem. Kinet., 48, 785–795, https://doi.org/10.1002/kin.21033, 2016.

Table 1: Regionally averaged mixing ratios of selected species (annual averages for 2010).

	NOAROM	*AROM*	ABSDIFF	RELDIFF
	mol/mol	mol/mol	mol/mol	%
OH				
AMA	2.861×10^{-14}	2.785×10^{-14}	-7.689×10^{-16}	-2.687
CAF	6.447×10^{-14}	6.086×10^{-14}	-3.616×10^{-15}	-5.608
EAS	4.712×10^{-14}	5.527×10^{-14}	8.147×10^{-15}	17.29
EUR	3.591×10^{-14}	3.852×10^{-14}	2.615×10^{-15}	7.283
EUS	5.629×10^{-14}	5.784×10^{-14}	1.553×10^{-15}	2.759
O_3				
AMA	2.979×10^{-8}	2.909×10^{-8}	-6.973×10^{-10}	-2.341
CAF	3.856×10^{-8}	3.712×10^{-8}	-1.440×10^{-9}	-3.733
EAS	3.124×10^{-8}	3.505×10^{-8}	3.807×10^{-9}	12.19
EUR	3.045×10^{-8}	3.033×10^{-8}	-1.250×10^{-10}	-0.4105
EUS	3.930×10^{-8}	3.904×10^{-8}	-2.604×10^{-10}	-0.6626
NO_3				
AMA	3.570×10^{-13}	3.483×10^{-13}	-8.678×10^{-15}	-2.431
CAF	2.105×10^{-12}	2.321×10^{-12}	2.163×10^{-13}	10.27
EAS	1.833×10^{-12}	1.949×10^{-12}	1.163×10^{-13}	6.346
EUR	1.280×10^{-12}	1.256×10^{-12}	-2.448×10^{-14}	-1.913
EUS	2.536×10^{-12}	2.488×10^{-12}	-4.802×10^{-14}	-1.894
HONO				
AMA	5.335×10^{-11}	5.349×10^{-11}	1.370×10^{-13}	0.2567
CAF	8.110×10^{-11}	8.227×10^{-11}	1.174×10^{-12}	1.447
EAS	1.152×10^{-10}	1.038×10^{-10}	-1.146×10^{-11}	-9.945
EUR	5.689×10^{-11}	5.604×10^{-11}	-8.429×10^{-13}	-1.482
EUS	4.415×10^{-11}	4.230×10^{-11}	-1.854×10^{-12}	-4.199
HNO_3				
AMA	1.515×10^{-10}	1.508×10^{-10}	-7.056×10^{-13}	-0.4657
CAF	4.957×10^{-10}	5.162×10^{-10}	2.048×10^{-11}	4.131
EAS	1.035×10^{-9}	1.169×10^{-9}	1.335×10^{-10}	12.89
EUR	3.985×10^{-10}	4.003×10^{-10}	1.855×10^{-12}	0.4656
EUS	6.706×10^{-10}	6.721×10^{-10}	1.505×10^{-12}	0.2244
HCHO				
AMA	5.217×10^{-9}	5.189×10^{-9}	-2.874×10^{-11}	-0.5509
CAF	3.468×10^{-9}	3.478×10^{-9}	9.392×10^{-12}	0.2708
EAS	1.322×10^{-9}	1.557×10^{-9}	2.348×10^{-10}	17.76
EUR	7.356×10^{-10}	7.708×10^{-10}	3.517×10^{-11}	4.781
EUS	1.911×10^{-9}	1.942×10^{-9}	3.096×10^{-11}	1.620
glyoxal				
AMA	1.473×10^{-10}	1.514×10^{-10}	4.120×10^{-12}	2.797
CAF	7.507×10^{-11}	1.169×10^{-10}	4.180×10^{-11}	55.68
EAS	3.077×10^{-11}	1.119×10^{-10}	8.112×10^{-11}	263.6
EUR	1.410×10^{-11}	3.271×10^{-11}	1.861×10^{-11}	132.0
EUS	6.217×10^{-11}	8.121×10^{-11}	1.904×10^{-11}	30.63
methyl glyoxal				
AMA	8.078×10^{-10}	8.021×10^{-10}	-5.711×10^{-12}	-0.7070
CAF	2.684×10^{-10}	2.802×10^{-10}	1.176×10^{-11}	4.383
EAS	5.081×10^{-11}	9.389×10^{-11}	4.308×10^{-11}	84.80
EUR	2.214×10^{-11}	3.157×10^{-11}	9.425×10^{-12}	42.57
EUS	1.938×10^{-10}	2.036×10^{-10}	9.750×10^{-12}	5.031