

Reply to RC2 on acp-2020-461

Taraborrelli *et al.*

December 16, 2020

Dear Alexander Archibald (Referee #2),

thank you for taking the time to review of our manuscript. It gave us the chance to improve the manuscript significantly.

Please find below a point-by-point response to your comments.

Description

Taraborrelli et al. provide an updated mechanism for the oxidation of aromatics in the EMAC model and a summary of the impacts of this update on key trace gases in the troposphere. This is a generally well written and well executed study but I have several minor comments in the attached pdf and a few more major comments before recommending publication.

Major comments

Comparison to observations is lacking which limits the sense I get that the changes are in anyway in the right direction. For example, the changes in surface ozone and NO₂ in EAS are large and I would imagine significant. It would be good to see how these compare with observations. Whilst I agree with the previous reviewers comments about model resolution and whilst there may well be structural errors in EMAC that mean that even with a better representation of the chemistry the comparison to observations is worse, I feel some comparison to observations is warranted.

Reply:

We agree with the referee that comparison with observations would strengthen and focus the manuscript. However, a comprehensive evaluation of the EMAC model with the complex organic chemistry (MOM) and against satellite retrievals of O₃ and NO₂ is in preparation and will be soon submitted for peer review. A first comparison of the model results with IASI-FORLI retrievals for ozone along with a detailed O_x budget is currently presented in Rosanka et al. (2020). The model results for tropospheric ozone, with the modified MCM chemistry of aromatics we present here, are clearly still too high with overestimates of up to 10 DU. This positive bias will be addressed by further improving existent parametrizations in EMAC like the dry deposition scheme (Emmerichs et al., 2020) and extending the representation of multiphase chemistry, which started with Rosanka et al. (2020), to deliquescent aerosols.

I also feel this will help focus the paper as currently it reads as one in which aromatics vs no-aromatics is the focus, but given we know aromatics are important (and abundant in urban environments) shouldn't the focus be Arom vs OnlyMCM? At least I find this comparison more interesting than Arom vs NoArom. It would be good if there were some figures (perhaps in an appendix) which compare the OnlyMCM and Arom scheme under idealised (Box model) conditions. Ideally this would be against laboratory data but I think even against some general scenarios it would be very useful to see how the differences implemented affect the results and then some sensitivity analysis could be performed I think quite straightforwardly to look at the impacts of some of these uncertain thermal-kinetic and photolytic processes.

Reply:

We thank the referee for this comment. Currently, we are not setup to compare box model simulations to lab data from chamber experiments. Our *modus operandi* is to obtain an intermediate and faithful reduction of a chemical mechanism like MCM that has been widely used and tested against lab measurements. We also believe that the differences in the results between AROM and onlyMCM are interesting to show. Instead of showing box model simulation results under idealized conditions, we think that showing the global distribution of the differences (spanning many possible scenarios) between AROM and onlyMCM simulations is a synthetic and useful way to visualize the deviations across a comprehensive set of chemical regimes. We therefore added an appendix to the manuscript to enhance the discussion of the differences between the MCM mechanism and our mechanism for the aromatics. In this appendix we briefly present the differences for the main oxidants OH, O₃ and NO₃.

Specific Comments

L13: Changes of what?

Reply:

We added "of trace gas levels" to the text.

L19: Is this a net loss? If not, is it a very important finding?

Reply:

This is a direct loss of ozone. As it is localized in the upper troposphere where benzene is transported and NO levels are generally low, this turns into a net loss of ozone. However, model setup used in this study did not have a comprehensive set of passive tracers that allows the classical tropospheric O_x budget to be computed. Nevertheless, we think that this result, the direct loss of ozone, is worth noting especially because it is clearly missing in all other global models with which the global impact of aromatics on ozone has been estimated to be positive, contrary to our study.

L31: This is too vague. There are specific definitions of aromaticity with implications for the chemistry of compounds in this class.

Reply:

We agree with the referee that we need to be more specific in this respect. Thus, we have changed the first sentence of the paragraph by stating that aromatics are unsaturated planar cyclic organic compounds with enhanced stability due to a strong electron delocalization.

L38: Add a reference for the toluene biogenic emissions.

Reply:

We added the reference to the first reported biogenic emission of toluene by Heiden et al. (1999).

L42: Is that true of all aromatics? i.e. benzene?

Reply:

We agree with the referee that it might sound odd to put benzene in the category of organic compounds that have a high reactivity. We have changed the relative sentence by removing the reference to the high reactivity and expressed in more neutral terms with a range of tropospheric lifetimes.

L46-50: There is a rich literature on many aspects of this chemistry which should be cited.

Reply:

We agree with the referee and we added the references to the review papers by Atkinson and Arey (2003) and Vereecken (2019). For the SOA formation from aromatics oxidation we now refer to Henze et al. (2008) and Lin et al. (2012).

L78: How were they added? i.e. what cross-sections and quantum yields used?

Reply:

We apologize for the lack of detail here. For the photolytic HONO-formation from nitrophenols the cross sections and quantum yield provided by Chen et al. (2011) are used by the JVAL and JVPP models (Sander et al., 2014) for calculating the j -values. We have modified the manuscript accordingly.

L89: Please be quantitative.

Reply:

We have added to the revised manuscript the information on the yields of glyoxal (60%) and methylglyoxal (40%) for toluene from Birdsall et al. (2010). We also specify now that these yields are for the non-radical terminating channels in the reactions with NO and HO₂.

L110: Please plot the data in nmol/mol to make things clearer for the reader.

Reply:

Yes, we now plot the data with mol/mol and the appropriate exponent for the range of values shown. We agree it was not clear before.

L118: Insert "surface" between these two words.

Reply:

Done.

L131-132: Can you be more specific on both the impact on the OH NH:SH ratio change and the impact on the methane lifetime.

Reply:

Referee #1 had a similar comment and 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.

L135-136: Has there been an increase in the flux through O₃+OH? I'm surprised given the OH has gone down in these regions.

Reply:

We thank the referee for spotting this inconsistency. Clearly, the simulation results do not support the statement on an increase in the flux of the O₃ + OH reaction in ozone-depleting regimes, e.g. over the ocean. We have removed OH from this explanation.

L141: Odd to ref. Fig 9 before 7 or 8. Re-order?

Reply:

Thank you for spotting this. The figures are reordered now.

L153: Can you confirm which definition you used in the analysis?

Reply:

Tropospheric burdens were reckoned using six different tropopause definitions (provided by the TROPOP submodel, see Jöckel et al. (2010) for details): 1,2) surfaces of O₃ mixing ratio of 125 and 150 nmol/mol, respectively, 3) WMO definition (WMO (1957)), 4) dynamic PV-based (3.5 PVU potential vorticity surface, sought within 50–800 hPa), 5) climatological (invariable zonal profile, i.e. $300-215 \times (\cos(\text{latitude}))^2$ hPa) and 6) the combined definition (WMO tropopause within 30°N–30°S, otherwise dynamic PV-based tropopause). The latter definition is used by default in EMAC and in this manuscript to report tropospheric budgets. Estimated changes to tropospheric O₃ burden are identical within 0.05% between the available definitions, which we conclude as robust against the definition used. We now put this information in the caption of Table 4.

L155: Is it widely acknowledged that it is “only” ozonolysis? And does the definition of loss change with different constructs of the O₃ budget (c.f. Bates and Jacob 2019)?

Reply:

According to the expanded definition of the odd oxygen budget by Bates and Jacob (2020), the loss ozone from reaction with phenoxy radical would count as half since RO₂ formation is counted with the “stoichiometric” coefficient 0.5 in the O_y family. This coefficient is justified in order to account for the effect the O(¹D) + H₂O reaction has on OH. However, the rationale and validity of this “stoichiometric” accounting for peroxy radicals is not clear. We agree that when ozone reacts with phenoxy radical close to the pollution sources the NO-to-NO₂ conversion by the resulting phenyl peroxy radical would largely compensate the ozone loss in question. However, in the upper troposphere where benzene is transported and where NO levels are usually low, the loss of ozone with phenoxy is a net loss.

L156: Perhaps add e.g., as this is just one models calculation.

Reply:

Done.

L161: Confirm if you mean ozone or odd-oxygen?

Reply:

We mean ozone.

L166-167: Can you quantify the relative contribution of these different pathways to the 200 Tg/yr O₃ (odd oxygen?) loss?

Reply:

We now realize that our formulations have been not clear and misleading. The 200-300 Tg/yr we give in the manuscript is the direct ozone loss in the reaction with (substituted) phenoxy radicals. What we wanted to express here was that the phenyl peroxy radical produced by reaction R3 enhances the NO₃ formation at night, which in turn enhances the O_x via the heterogeneous loss of N₂O₅. Having no detailed passive tracers for computing the O_x budget in this study, we cannot quantify the strength of the O_x destruction we describe. We now make this clearer in the revised manuscript.

L174: But the way you have written R1 suggests that phenoxy radicals are not formed (instead butenedial is formed).

Reply:

Indeed R1 destroys the aromaticity of the molecule and therefore any possibility to form further (substituted) phenoxy radicals. Unfortunately, we have not explicitly mentioned that in MCM (AROM and onlyMCM simulations) the reactions of the simplest nitrophenol (HOC6H4NO2) yield a nitrophenoxy radical which is assumed to react with O₃ and NO₂ like phenoxy radical (C6H5O). We have made this point clearer in the revised manuscript.

Table 3: Can you confirm that these are area weighted? The surface ozone seems a bit high compared to other models I've seen.

Reply:

Yes, they are. We have added this information in the table caption. We share the impression of the reviewer that the model computes high levels of surface ozone. We are addressing the general overestimation of tropospheric ozone by, among others, improvements of the dry deposition scheme lacking the non-stomatal sink (Emmerichs et al., 2020) and the explicit modelling of the ozone sink in cloud droplets (Rosanka et al., 2020) and deliquescent aerosols.

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