

A review report on the revised manuscript of “Global tropospheric hydroxyl distribution, budget and reactivity” by Lelieveld et al., 2016.

In this revised manuscript, the authors present, in great details, their simulation results of OH, HO₂, OH reactivity and OH recycling efficiency using a new chemical mechanism called “MOM”. This is certainly an important topic and the manuscript is interesting, very detailed and is well written. However, I have some major concerns, which are:

1. The manuscript is aiming at informing the scientific community that the MOM solves the known biases in OH, especially, over low NO_x, high isoprene regions (e.g., over the Amazonia), but without any experimental scientific evidences. Reaction rates and branching ratios can only be verified in smog chambers.
2. The unverified new reactions and secondary OVOCs in the MOM is a fundamental issue in the article. The previous MIM1 and MIM2 (Taraborelli et al., 2009) are reduced mechanisms from well-known MCMv3.1, which are the ones that have been subject to validations in the mentioned EMAC literatures. As of MIM3 and MOM, there are no validation studies and/or sufficient evidence that these chemical mechanisms would hold compared to laboratory, smog chambers experiments or field measurements or even other mechanisms, e.g., MCMv3.3. Further detailed validations are necessary **before** scientific conclusions can be made based on these, yet, theoretical schemes.
3. The information on MOM in Page 12, lines 12-21 is the most important part in the manuscript and I suggest that the authors move it to the very beginning of the discussion. With these infos, the authors are encouraged to include some validation/comparison to understand the significance of these updates on the results. Also how these updates compares to the updates in the MIM3 (Taraborelli et al., 2012)?
4. Why only MOM captures this higher OH recycling in the free troposphere? Recent measurement-modeling studies (e.g., Nicely et al., 2016 and Anderson et al., 2015) found that global models underestimate OH by 20-30% related to uncertainties in the underestimated NO_x levels as well as HCHO in the upper troposphere. **Thus, the “new” increased OH reactivity in the MOM, without accounting to these factors, may cause an excessive recycling and thus unnecessary higher production of OH.** This is a primary concern given that MOM is yet not validated with measurements.

General comments:

Page 1, line 6: ozone photolysis is the primary OH source on global scale; on regional scale there are other important sources (e.g., Stone et al., 2012). Authors may correct the sentence such as: insert “is mainly: after “the former”.

Page 1, line 8: Why did the authors use the EMAC model as “general circulation model” and not in the CTM mode (i.e., using prescribed meteorology), typically used for chemistry studies to isolate the dynamics effects?

Page 1, line 9: Perhaps the authors can shortly elaborate, why the MOM produces higher OH reactivity? e.g., higher concentration/number of VOC oxidation products..etc, why? Experimental evidences?

Page 1, line 11:

The primary questions here are: Why only MOM captures this higher OH recycling in the free troposphere. Recent measurement-modeling studies (e.g., Nicely et al., 2016 and Anderson et al., 2015) found that global models underestimate OH by 20-30% related to uncertainties in the underestimated NO_x levels as well as HCHO in the upper troposphere. Thus, the “artificially” increased OH reactivity in the MOM, without accounting to these factors, may cause an excessive recycling and thus unnecessary higher production of OH. This is a primary concern given that MOM is yet not validated with measurements.

Page 1, line 13: If the authors mean by “OH is buffered” that OH is not sensitive to changes in VOC of OH precursor levels, why is that? If S (VOC+OH→HO₂+NO→OH) is higher than primary OH productions (e.g., O(1D)+H₂O=OH), it is because of the high VOC and NO load, and the atmosphere should then be sensitive to primary OH sources (the limiting factor). Thus any increase or decrease in the primary OH precursors should affect OH levels. This is important, since the inclusion of any additional sources (e.g., Nicely et al., 2016, Anderson et al., 2015) to the MOM will disturb the current budget, again, which is not experimentally verified.

Page 1, line 14: OH primary formation (i.e, form O₃ photolysis) is the primary source of OH, though much smaller than the secondary formation. Thus, OH primary formation is not “complementary” to the secondary formation, i.e., without OH primary formation, OH will be depleted with time (via HO₂+O₃, HO₂+HO₂, OH+NO₂, ..etc). The authors are advised to revise the statement in line 14.

Page 1, line 21: What about other primary sources of tropospheric OH, e.g., alkene ozonolysis, (e.g., Stone et al., 2012)?

Page 2, line 17: The statement “In air that is directly influenced by pollution emissions S is largely controlled by nitrogen oxides (NO+NO₂ =NO_x)” is not clear. In highly polluted urban conditions, ozone photochemical formation, which is the secondary product of S, is typically VOC limited, since NO emissions is too high compared to HO₂. Authors are advised to elaborate here, what is the source of this info's, examples? Properly the authors meant “high isoprene emissions”?

Page 2, line 25: What is “self-limiting”?? At high NO_x levels (polluted conditions), NO₂ is a permanent sink of OH.

Page 3, line 26: how this new MOM would compare to MCMv3.3.1 (Jenkin et al., 2015) or to measurements?

Page 3, lines 31-33: Why the authors decided to use EMAC GCM as opposed to the CTM modes, typically used in atmospheric chemistry studies. How the authors would account for dynamics effects on their results in the case of GCM?

Page 4, lines 20-25: The MIM1 and MIM2 are considered as reduced mechanisms from MCM (Taraborelli et al., 2009), which are the ones that have been subject to validations in the mentioned EMAC literatures. As of MIM3 and MOM, there are no validation studies and/or sufficient evidence that these theoretical mechanisms would hold

compared to measurements. Further validations are needed before further scientific conclusions can be made based on these pure theoretical studies.

Page 5, line 10, 13: Since the simulation are performed for the year 2013, not any further, why the authors decided to use the RCP8.5, not, for example, a historical emissions scenarios, which should be available by the year 2016?

Page 7, lines 23-29: The authors should mention that these OH distributions are based on “annual mean” and that seasonal OH distributions are different. For example, in the NH extra-tropics, OH in the MBL is not equal to that in the CBL, during July (Figure S1), otherwise the discussion is misleading. Authors are also advised to show the seasonal distribution instead, as in Figure 2 for nighttime OH.

Page 7, lines 17-18: the authors mentioned “partly”, what other sources could be, e.g., higher O3 photolysis?

Page 7, lines 30-32: So, here the authors mentioned the alkenes ozonolysis, therefore, they also need to mention it along with other OH sources in the introduction.

Page 8, lin15-16: The statement is not clear. If sources of OH were high, OH would not have been depleted while HO2 is high. Would it be clearer to say that the reason for high HO2 but low OH is the low NOx condition, under which HO2 recycling efficiency is too low?. If OH is high because of the new introduced high OH recycling in MOM, then the authors should use this occasion to discuss why their new chemical mechanism works here..

Page 8, line 17: could the authors provide reference for the Strong NOx emissions from petroleum industry in the Gulf of Mexico?

Page 9, lines 21-23: This is the first statement that mentions comparison with previous mechanism or models, very briefly though!

Page 9, lines 26: Add the standard deviation, i.e. Error of the mean lifetime of methane.

Page 9, line 31, which observation-derived estimates, reference(s)?. As of Prinn et al. (2005), the mean is 10.2 years.

Page 10, lines 7-8: Again here, the authors very briefly mention why MOM is different from other models, How the “MOM mechanism more efficiently recycles OH than other VOC chemistry schemes applied in global models”?, How reasonable is this approach, compared to laboratory and field measurements of these enhanced recycling reaction??

Page 10, lines 20-30: Again, it is difficult to conclude a scientific values from these numbers without comparison and contrasting with measurements, previous mechanisms (e.g., MIM2) or MCMv3.1, especially that the authors claims that this is a new advanced MOM?

Page 12, lines 12-21 to Page 13, line 18: Here we go; actually this part is the most important part in the manuscript. Ok, so now, the authors need to add some validation/comparison to understand the relevance of these updates on the results. Also how these updates compares to the updates in the MIM3 (Traborelli et al., 2012)?

Fig. 9: correct the caption.

References:

Anderson D.C., et al.: A pervasive role for biomass burning in tropical high ozone/low water structures, Nature communication, 7, 10267, DOI: 10.1038/ncomms10267, 2015.

- Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, *Atmos. Chem. Phys.*, 15, 11433-11459, doi:10.5194/acp-15-11433-2015, 2015.
- Nicely, J. M., et al., An observationally constrained evaluation of the oxidative capacity in the tropical western Pacific troposphere, *J. Geophys. Res. Atmos.*, 121, 7461–7488, doi:10.1002/2016JD025067, 2016.
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- Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO₂ radicals: field measurements and model comparisons, *Chem. Soc. Rev.*, 41, 6348, doi:10.1039/c2cs35140d, 2012.
- Taraborrelli, D., Lawrence, M. G., Butler, T. M., Sander, R., and Lelieveld, J.: Mainz Isoprene Mechanism 2 (MIM2): an isoprene oxidation mechanism for regional and global atmospheric modelling, *Atmos. Chem. Phys.*, 9, 2751-2777, doi:10.5194/acp-9-2751-2009, 2009.