

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.

Reply: We thank the reviewer for emphasizing the importance of experimental work and smog chambers. We agree, and for that reason have performed studies in our lab, to which we refer in Sect. 2 (e.g., Groß et al., 2014a,b), and also refer to work in other labs (e.g., Paulot et al., 2009; Crouse et al., 2012, 2013; Fuchs et al., 2014; Peeters et al., 2014). We have tested our isoprene degradation mechanism in the EUPHORE reaction chamber (Nölscher et al., 2014), leading to important improvements. Our group is one of few who have performed measurements over tropical forests, showing experimentally that OH recycling in isoprene chemistry over the Amazon is a prerequisite to explain observed OH concentrations, which has been confirmed by similar measurements in S-E Asia (Pugh et al., 2010). These experimental studies have been complemented by theoretical studies in our group by Vereecken and co-workers. Hence we do not agree that this work is without experimental evidence.

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.

Reply: Our isoprene mechanism has been a complement to the MCMv3.2 mechanism, as the latter was developed with a focus on anthropogenic emissions, and we tested the scheme experimentally in Nölscher et al. (2014). Unlike other isoprene oxidation mechanisms in use, the scheme in MOM has been tested. The critical reactions involve H-migration within oxygenated reaction products, which are not unverified, as indicated above. Our aromatics scheme has been tested against the MCMv3.3 mechanism (Cabrera-Perez et al., 2016). The latter reference is new and also used MOM; we have added this reference to the revised manuscript. Since it is not possible to test all >1,600 reactions in our scheme experimentally, we have included the entire list to the supplement, for scrutiny in the community. This follows the philosophy of the MCM, which similarly includes reactions that have not been verified experimentally. While we do not agree with the referee that there are no validation studies, we do agree that further validation is necessary. However, this can hardly be a prerequisite for our model study, which has the character of putting forward a theory that can be falsified by experiments.

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)?

Reply: In Sect. 6 we explain the buffering mechanisms. By moving the paragraph on OVOC buffering to the beginning of the discussion the order of explanations would be interrupted. However, we agree that it would be helpful to have some of this information earlier in the paper. Therefore, we included the following sentence to p.4, l.17: “When the OH concentration is low, its formation is maintained by photo-dissociation of HPALD, while at high OH concentration its sink reaction with HPALD gains importance.” We will follow the encouragement of the reviewer by publishing a follow-up paper by Taraborrelli et al., which will be submitted to ACP soon. Experimental evidence of the revised role of h-shifts, leading to HPALD, can be found in Nölscher et al. (2014).

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.

Reply: We thank the reviewer for pointing to the interesting publications from the Anderson group. However, Anderson et al. (2016) did not address OH but rather O₃, suggesting that biomass burning, notably in topical Africa and SE Asia, is a dominant source. Both papers make use of aircraft measurements during the CONTRAST campaign, and data of O₃, CO, NO, HCHO, H₂O, C₃H₈, CH₄, C₅H₈, CH₃COCH₃, CH₃OH and CH₃CHO mixing ratios, and J(O1D) and J(NO2) are reported. OH and HO₂ radicals, nor tracers that could constrain biogenic VOC chemistry, were measured. The empirically based OH column (OH^{COL}) reported by by Nicely et al. (2016) was obtained by constraining a chemical box model. Subsequently, the empirical OH^{COL} concentrations were compared with CTMs, indicating that these models underestimate OH^{COL}, while they also underestimate NO_x. The final conclusion by Nicely et al. (2016) was that “our calculations do not support the prior suggestion of the existence of a tropospheric OH minimum in the tropical western Pacific, because during January–February 2014 observed levels of O₃ and NO were considerably larger than previously reported”. We do not see how this interpretation of data over the tropical Pacific Ocean, as remote from biogenic VOC emissions as conceivable in the easterly trades, might indicate that MOM may lead to excessive recycling and unnecessary higher production of OH. Perhaps some of the model underestimated NO indicated by Nicely et al. (2016) is related to the release from reservoir species in which VOCs play a role. We will look into this possibility in future work.

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”.

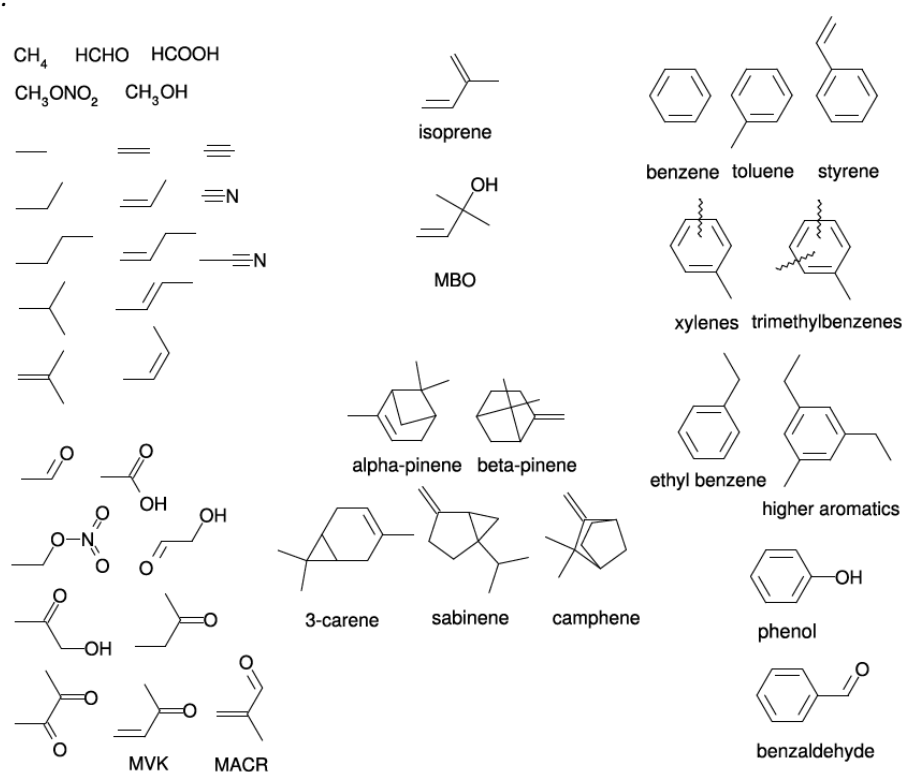
Reply: done

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?

Reply: In this work EMAC, which is a chemistry-general circulation model, was indeed used in the CTM mode. We have highlighted this in the manuscript, referring to Deckert et al. (2011).

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?

Reply: The main reason why MOM predicts higher OH reactivity is the large number (43) of primarily emitted VOCs that are accounted for (see Figure below). Furthermore, the degradation of the oxidation products is continued to the final product CO_2 , and the reactivity of the reaction intermediates can be large. Another reason for the increased OH reactivity modeled with MOM is due to the use of an updated Structure Activity Relationship (SAR) for estimating the rate constants for OH (Nölscher et al., 2015). This SAR will be detailed in the manuscript of Taraborrelli et al. (in preparation).



Experimental evidences?

Reply: See replies above.

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.

Reply: This repeats the remarks of comment 4 above. We have replied accordingly. We object to the tendentious remarks of “artificially increased OH reactivity” and “excessive recycling and unnecessary higher production of OH”, which are unfounded.

Page 1, line 13: If the authors mean by “OH is buffered” that OH is not sensitive to changes in VOC or OH precursor levels, why is that? If S ($\text{VOC} + \text{OH} \rightarrow \text{HO}_2 + \text{NO} \rightarrow \text{OH}$) is higher than primary OH productions (e.g., $\text{O}(1\text{D}) + \text{H}_2\text{O} = \text{OH}$), 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.

Reply: We apologize but do not understand this comment. Does the referee mean that the current budget is not experimentally verified? We would be eager to learn which budget has been experimentally verified.

Page 1, line 14: OH primary formation (i.e., from O_3 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 $\text{HO}_2 + \text{O}_3$, $\text{HO}_2 + \text{HO}_2$, $\text{OH} + \text{NO}_2$, ..etc). The authors are advised to revise the statement in line 14.

Reply: We have added “primary and secondary” to l.14.

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

Reply: As shown in the supplement, these reactions are included in our mechanism. In some cases such reactions could contribute to boundary layer OH formation at night, while they do not play a significant role in the global OH budget, as discussed in our manuscript. Stone et al. (2012) discuss these reactions primarily because they can lead to spurious OH formation in instruments that apply the LIF-FAGE technique.

Page 2, line 17: The statement “In air that is directly influenced by pollution emissions S is largely controlled by nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$)” 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 HO_2 . Authors are advised to elaborate here, what is the source of this info’s, examples? Properly the authors meant “high isoprene emissions”?

Reply: We believe that this sentence is clear and that it is in line with the well-known fact that in polluted air OH recycling is dominated by the reaction $\text{NO} + \text{HO}_2$ (R7). It has nothing to do with isoprene emissions.

Page 2, line 25: What is “self-limiting”?? At high NO_x levels (polluted conditions), NO_2 is a permanent sink of OH.

Reply: It means that reaction R7 recycles OH, but reaction R10 becomes such a large sink of OH that it limits the net OH production. This is well known and elaborated in textbooks.

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

Reply: The isoprene mechanisms in MOM and MCMv3.3 have much in common, as will be elaborated by Taraborrelli et al. (in preparation). Perhaps the referee can check with the group of Jenkin to verify about experimental validation against smog chamber experiments.

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?

Reply: This question has been answered above.

Page 4, lines 20-25: The MIM1 and MIM2 are considered as reduced mechanisms from MCM (Taraborrelli 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.

Reply: This comment has also been replied to in the above replies.

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?

Reply: Such scenarios are not available, and are not fundamentally important for the present study.

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.

Reply: These distributions do not refer to annual mean, but to geographical mean in the MBL and CBL, as indicated in the text. The seasonal dependence is not relevant for this discussion.

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

Reply: The point here is that the enhanced OH is related to the convective transport of VOC emissions and NOx from lightning. To express this more clearly we start the sentence with "The relatively high OH.." and have dropped the word "partly".

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.

Reply: As indicated above, this is not a major OH source. Instead of mentioning it in the introduction, it suffices that it is discussed in Sect. 3.

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 NO_x 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.

Reply: The OH sources as well as sinks are strong, so that overall OH is not very high, but since OH is converted into HO₂, total HO_x can still be high. Why would the HO₂ recycling efficiency be too low? We do not understand this. In MOM the OH is higher over the forest than most other models that do not account for OH recycling in isoprene chemistry. This was shown by Taraborrelli et al. (2012) and Nölscher et al. (2014) based on MIM3. This version of the isoprene chemistry is also part of MOM.

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

Reply: We have added the reference Ren et al. (2013) for the Mexican and Lelieveld et al. (2009) for the Persian Gulf.

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

Reply: ok

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

Reply: A standard deviation here would not give additional information, as only the year-to-year standard deviation can be calculated (i.e., an indication of OH inter-annual variability). Hence it would not add information on the range of the methane lifetime. It may also confuse the reader as later in the text the methane lifetime from literature is mentioned, together with the standard deviation from the model ensemble, which is a different metric.

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

Reply: We refer to Naik et al. (2013) who included Prinn et al. (2005) and others for their estimate of "observation-based estimates". Our group has also been involved in such estimates, expressing caution with the interpretation (see Krol and Lelieveld, 2003; Montzka et al., 2011).

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??

Reply: Why does the referee keep repeating the same comment? We explain this in our manuscript, showing that the account of higher generation reaction products in VOC chemistry (often truncated or simplified in models) leads to higher and more realistic OH reactivity and OH recycling. Our isoprene oxidation scheme is the first (and presently the only one) that was tested in the EUPHORE reaction chamber (Nölscher et al., 2014).

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?

Reply: see above.

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)?

Reply: see above

Fig. 9: correct the caption.

Reply: done