

Interactive comment on “Global tropospheric hydroxyl distribution, budget and reactivity” by J. Lelieveld et al.

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This paper discusses global OH. The paper is well-written and reads smoothly. Illustrations and supplement give a large amount of interesting information. Basically, the paper describes the update of the Mainz-Isoprene-Mechanism (MIM) to MOM and additionally studies the primary formation of OH, the OH recycling (secondary OH formation) as well as HO₂. Having read the paper with great pleasure, I looked back and wondered what I learned. This uncovered several fundamental weaknesses of the paper, which are outlined below:

(1) How does MOM change the OH budget? The paper concentrates on the current model, run for 2013. But I would like to know fundamental things like: By how much did OH increase by including low-NO_x recycling? Is the OH abundance still compliant

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with the CH₄ lifetime and/or methyl chloroform analysis?

Reply: In the revised manuscript we will present sensitivity simulations to demonstrate the influence of the three main OH recycling mechanisms. This will show their influence on OH, including the recycling under low-NO_x conditions. It will be interesting to see the difference of OH recycling under high-NO_x and low-NO_x conditions. In Sect. 5 we discuss the CH₄ lifetime in view of results by other models, as presented by Naik et al. (2013). In the revised manuscript we will extend this discussion, including the lifetime of methyl chloroform.

(2) Why should we, apart from the OH budget, also analyze the HO₂ budget? The paper analyses the HO₂ budget, but without much motivation. Concerning OH, one could argue that this is the “cleansing agent” of our atmosphere. Why HO₂, not RO₂, or other short-lived species of which the abundances are determined by local chemistry?

Reply: The HO₂ budget is included because the main OH conversions in atmospheric chemistry directly relate to HO₂ (e.g., reactions with NO_x, CO). HO₂ is critically important for OH recycling, which is a central topic of our paper. Field and laboratory measurements often address both OH and HO₂, e.g., by reporting ratios. By providing global concentration distributions and budgets of both molecules in our paper, we may help guide and interpret radical measurements, while the resulting data in turn provide important constraints for HO_x and OH studies. In the revised manuscript we will more explicitly motivate why HO₂ has been included.

(3) The paper discusses concepts like “tele-connections” and “buffering” without proper definitions. Maybe the largest complaint from my side. Earlier work by the authors introduced the “recycling probability”, which has at least a proper definition (the probability that OH, once formed, is recycled). However, buffering and tele-connection have not been defined in the paper and hence give freedom to use these terms for everything that is or cannot be fully quantified. I suggest that the authors at least define and quantify terms like “buffering”. One handle could be to actually use perturbations (e.g. the

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transition from MIM to MOM) to investigate where OH is “buffered”. My further remarks below identify parts of the text where the text was specifically vague.

Reply: We agree that these concepts could be defined more clearly. The concept “tele-connection” is not centrally important in the present context and will be removed from the revised manuscript. However, the concept “buffering” is important and will be discussed more extensively in the revision. This discussion will make use of the model perturbation experiments presented by Lelieveld et al. (2002), i.e., applying NO_x and CH₄ perturbations and computing the impact on OH. This showed that at an OH recycling probability of 60% or higher, these perturbations have negligible influence on OH. We argue that this can be considered as a buffered chemical system. In the revised manuscript we will also present sensitivity calculations in which the three main OH recycling mechanisms will be switched off one-by-one, which will quantify their role in OH recycling and buffering.

Like stated above, the paper lacks quantitative analysis. In section 4 the HO₂ budget is discussed, however, with very little justification (rather vague statements appear: “transport processes influence HO_x through longer-lived precursors and reservoir species such as O₃ and OVOC”). The authors write: “Our results suggest that HO_x is highest over tropical. . .and OH sinks are large”. This would call for an analysis in terms of the main photochemical path-ways (i.e. RH, CO shifting the HO_x balance towards HO₂/RO₂, and NO/O₃ shifting the balance back through NO/O₃ + HO₂ OH + NO₂, some hints of this analysis in line 26, page 7). Certainly it must be possible to provide a somewhat deeper analysis! Without such an analysis I see very little motivation to show the HO₂ budget in such detail. One driver would be the availability of atmospheric observations of HO₂, but this is handled by one reference in a short sentence.

Reply: For the HO₂ budget, see above. We agree that it would be interesting to study photochemical pathways, and we will try to deepen the analysis, however, without losing scope and our global view of OH, as indicated in the title. Since OH and HO₂ are

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often studied together for good reason, it makes sense to present both. For example, the lifetime of HO₂ helps evaluate the efficiency of OH recycling, which we will make more explicit in the revised manuscript. We believe that providing the budget and distribution of HO₂ helps appreciate that of OH.

Moreover, many statements are made from which the quantitative nature is unclear. Is this speculation, on backed by calculations? Examples: Page 6, lines 26-30: “is partly related to...are a near source aloft” Page 7, lines 28-31: “The efficient atmospheric transport...across altitudes”

Reply: The interpretation of results does not necessarily always needs to be quantitative. This paper aims at conceptual understanding of the atmospheric oxidation efficiency. Certainly this is not speculation. We will refer to previous work that shows the important role of lightning over Central Africa: Tost, H., P. Jöckel and J. Lelieveld (2007) Lightning and convection parameterizations – uncertainties in global modeling. *Atmos. Chem. Phys.* 7, 4553-4568. For the role of stratosphere – troposphere exchange of ozone we will refer to Lelieveld, J. and F.J. Dentener (2000) What controls tropospheric ozone? *J. Geophys. Res.* 105, 3531-3551.

Vague statements are also given on page 9, lines 7-9: The effective (?) difference in oxidation capacity (is this OH or HO_x, how defined?)...is a factor of ten, which is close to the extra-tropical seasonal cycle of HO_x. This is smaller than..., indicative of the important role of secondary (OH) formation. With this statement, the authors seem to suggest that the gradient in OH is linked to the extra-tropical seasonal cycle of HO_x, and smaller than the gradient in primary production. It took me a while, however, to decipher this sentence, and once again miss some kind of “interpretation framework” that would deepen general understanding. The main message seems to be that the seasonal cycle in OH is smaller in magnitude than the seasonal cycle in primary OH formation, a statement that is not totally surprising but for now lacks quantitative explanation and seems poorly connected to concepts like buffering.

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Reply: The bottom line is that OH recycling can partly compensate the lack of primary OH production in locations and seasons where actinic radiation or water vapor concentrations are low. This is not at all vague, and fits our interpretation framework. However, we agree that the indicated sentence may be difficult to understand. In the revised manuscript we will express this more clearly and elaborately.

Other remarks: Page 4: Results have been evaluated (page 4, line 22): references are of 2010, after which substantial updates took place in isoprene chemistry. So that must have been different results? Please be clear about validation. The CO and O3 comparisons in the supplement do not look very convincing.

Reply: With the sensitivity simulations indicated above, the role of isoprene chemistry will become clearer. We expect to submit a comprehensive ACP manuscript about the new isoprene chemistry soon (Taraborrelli et al., in preparation), and we will update the references.

Page 2, line 23: P,S, and G have unit (moles / year), please provide.

Reply: will be done.

Page 2, line 32: “observation-based studies”. I think it is good to mention specifically that this is based on methyl chloroform, because this suggests “OH observation-based studies”.

Reply: will be done.

Page 4, line 11: “in future”. This suggests that this study is based on the complete mechanism. Please say so directly, and mention that this is computationally heavy, and prevents multi-year simulations (i.e. restricting the current study to one year at T42/L31 resolution).

Reply: will be done.

Page 4, line 27: natural VOC emissions are 747-789 TgC/year, but we are discussion

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2013 results only. So, it would be correct to give only the 2013 value here.

Reply: will be done.

Page 5, line 11: “may be relevant”. I would prefer “are relevant”.

Reply: will be done.

Page 5, line 18: “mean tropospheric OH”: unclear how troposphere is defined (from the supplement it is clear that a dynamical tropopause is calculated).

Reply: will be improved.

Page 6, line 1: “being the main reason”. I wonder if this is true. OH in the extra-tropics is much lower than in the tropics. I cannot assess the NH/SH in the tropics, but the influence of “ITCZ”-weighting suggests a leading role of tropical OH.

Reply: This is correct, as shown in many publications.

Page 6, top paragraph. This is now rather confusing. The numbers quoted seem to refer to volume-weighted OH, which puts unrealistic weight on the stratosphere, leading to OH-parity in the integrated atmosphere. This is likely due to parity in the sinks (CO, CH₄, etc.) which show much less NH/SH differences in the stratosphere. But I would argue that the mass (or CH₄/MCF weighted) OH is the quantity to be analyzed here (see paper Lawrence et al., 2001). Table S15 clearly shows the impact of the selected weighting procedure.

Reply: It is common to provide the volume weighted OH. To prevent interpretation issues we also give the other metrics suggested by Lawrence et al. (2001). To prevent unrealistic weight on the stratosphere we present results for the troposphere and the lower stratosphere separately.

Page 8, line 30-31 and further: Here the authors suggest that the slow rate of SO₂ + OH “serves a purpose in the Earth system” (??). This is rather vague again. What I get from it is that, if the reaction rate would be faster at low temperatures, tropical

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volcanic eruptions would deplete OH completely around the tropopause. This, in turn, would be a threat to the ozone layer, because O₃ destroying halocarbons (natural, anthropogenic?) would freely pass the tropopause. If the authors want to suggest that the ozone layer would not have been formed with a faster SO₂ + OH reaction rate in cold conditions in a volcanically-active early Earth, they could simply quantify the impact in their model. Without further elaboration, this side note is clearly out of scope here.

Reply: We will remove this paragraph from the revised manuscript.

Page 9, lines 31-31: G is the same over the continent as over the oceans, and this would show that OH is buffered through processes in the FT. Figure 7 misses units (mol/m²/year?). This statement implies that the contrast in G of MBL and CBL is large, but these plots are not provided in the supplement. The text mentions that G is on average 3x larger in the CBL than in the MBL, and likely the S-term in G dominates, because the contrast in P is small. Nevertheless, the authors write on page 10, line 7, that S is similar over oceans and continents (in contrast to what figure 7 shows). Page 10, line 13. This actually contributes to OH buffering. Since there is no actual definition of what “buffering” is, this remains a vague statement. A definition on internet says: “Something that lessens or absorbs the shock of an impact.” In the context of OH being driven by primary and secondary formation pathways, I do not see how the “impact” is defined. Only if anything reducing primary production (O₃, radiation, water vapor) would result in enhanced recycling of OH, I would see a buffer. A proper definition and analysis of the “buffer” concept would greatly enhance the readability of the paper.

Reply: We will include units, and relate the buffering to a definition that will be given in the revised manuscript, as indicated above. We will revise the text in this context.

Page 10, line 24. Is the R₂ defined for the log-scale or the linear scale? This suggests linear.

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Reply: Correct, this refers to a linear relationship between variables.

Page 10, line 29. Here a new concept is introduced, named a recycling efficiency, defined as $(S-P)/G$. Together with $G = S + P$ and $r = 1-P/G$, it seems to me that this representation is abundant, and further complicates the discussion. The information in the left and right panels of figure 9 is therefore similar. I would suggest to avoid further definitions.

Reply: In the revised manuscript we will remove the recycling efficiency (left panels of Fig. 9).

Page 11, line 4: “The chemical buffering mechanisms include the dominant though self-limiting effect of NO_x on OH formation in polluted air.” Closer to a definition, but now introducing “chemical” and presumably also “transport-related” buffers. It has been shown that at high NO_x levels, the chemical system can enter a “run-away” regime (so definitely not buffered), in which fresh NO consumes O₃ and the formed NO₂ reacts with OH. Given the large grid-cells in EMAC, this effect will likely not occur, but bringing this mechanism as a chemical buffering mechanism seems incorrect to me. Again, the paper would profit from a clear definition and interpretation framework addressing “buffering”.

Reply: Runaway conditions have been shown in box modeling studies, while in the real atmosphere such conditions are not observed as they are quickly diluted by transport and mixing processes. This illustrates the importance of transport. Such conditions would also have reduced OH recycling probability and therefore not qualify as buffered. Please realize that even a buffered system can be perturbed so heavily that the buffering capacity is exceeded. Even if runaway conditions would occur locally, they would be of limited duration and not relevant globally. As indicated above, we will provide a clear definition of buffering in the revised manuscript.

Page 11, discussion figure 10. Now it seems that “ r ” is defined as “buffer”, because figure 10 illustrates how OH is buffered on the local and global scales. Further the

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authors write: “the complementarity of the three mechanisms in remarkable”. Is this not the case by definition as “r” is being decomposed?

Reply: In the revised manuscript we will remove the word remarkable and use “r” to define buffering, as indicated above.

Page 12, line 15: “Physical-chemical tele-connections”. How are these defined? I am not a fan of the word “teleconnection” because it refers to something that is only vaguely understood (we see a correlation at large distances, but we do not really understand precisely why this correlation is present). In this case atmospheric transport mixes long-lived gases through the atmosphere (O₃, CO, CH₄, PAN, . . .) thereby influencing remote regions with “signals” of photochemistry that occurred e.g. over regions with high natural or anthropogenic emissions (e.g. last sentence of the manuscript). This is well-understood, operates on short and long distances, and is therefore definitely not a tele-connection.

Reply: We will avoid the word tele-connection in the revised manuscript.

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