

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

### **Anonymous Referee #1**

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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 HO<sub>2</sub>. 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<sub>x</sub> recycling? Is the OH abundance still compliant with the CH<sub>4</sub> lifetime and/or methyl chloroform

C1

analysis?

(2) Why should we, apart from the OH budget, also analyze the HO<sub>2</sub> budget?

The paper analyses the HO<sub>2</sub> budget, but without much motivation. Concerning OH, one could argue that this is the “cleansing agent” of our atmosphere. Why HO<sub>2</sub>, not RO<sub>2</sub>, or other short-lived species of which the abundances are determined by local chemistry?

(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 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.

Like stated above, the paper lacks quantitative analysis. In section 4 the HO<sub>2</sub> budget is discussed, however, with very little justification (rather vague statements appear: “transport processes influence HO<sub>x</sub> through longer-lived precursors and reservoir species such as O<sub>3</sub> and OVOC”). The authors write: “Our results suggest that HO<sub>x</sub> 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<sub>x</sub> balance towards HO<sub>2</sub>/RO<sub>2</sub>, and NO/O<sub>3</sub> shifting the balance back through NO/O<sub>3</sub> + HO<sub>2</sub> OH + NO<sub>2</sub>, 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 mo-

C2

tivation to show the HO<sub>2</sub> budget in such detail. One driver would be the availability of atmospheric observations of HO<sub>2</sub>, but this is handled by one reference in a short sentence.

Moreover, many statements are made from which the quantitative nature is unclear. Is this speculation, or 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"

Vague statements are also given on page 9, lines 7-9: The effective (?) difference in oxidation capacity (is this OH or HO<sub>x</sub>, how defined?) ...is a factor of ten, which is close to the extra-tropical seasonal cycle of HO<sub>x</sub>. 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<sub>x</sub>, 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.

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 O<sub>3</sub> comparisons in the supplement do not look very convincing.

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

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

C3

studies".

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).

Page 4, line 27: natural VOC emissions are 747-789 TgC/year, but we are discussing 2013 results only. So, it would be correct to give only the 2013 value here.

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

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

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.

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, CH<sub>4</sub>, etc.) which show much less NH/SH differences in the stratosphere. But I would argue that the mass (or CH<sub>4</sub>/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.

Page 8, line 30-31 and further: Here the authors suggest that the slow rate of SO<sub>2</sub> + 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 volcanic eruptions would deplete OH completely around the tropopause. This, in turn, would be a threat to the ozone layer, because O<sub>3</sub> destroying halocarbons (natural, anthropogenic?) would freely pass the tropopause. If the authors want to suggest

C4

that the ozone layer would not have been formed with a faster  $\text{SO}_2 + \text{OH}$  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.

Page 9, lines 31-31:  $G$  is the same over the continent as over the oceans, and this would show that  $\text{OH}$  is buffered through processes in the FT. Figure 7 misses units ( $\text{mol}/\text{m}^2/\text{year}$ ?). 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  $\text{OH}$  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  $\text{OH}$  being driven by primary and secondary formation pathways, I do not see how the “impact” is defined. Only if anything reducing primary production ( $\text{O}_3$ , radiation, water vapor) would result in enhanced recycling of  $\text{OH}$ , I would see a buffer. A proper definition and analysis of the “buffer” concept would greatly enhance the readability of the paper.

Page 10, line 24. Is the  $R_2$  defined for the log-scale or the linear scale? This suggests linear.

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.

Page 11, line 4: “The chemical buffering mechanisms include the dominant though

C5

self-limiting effect of  $\text{NO}_x$  on  $\text{OH}$  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  $\text{NO}_x$  levels, the chemical system can enter a “run-away” regime (so definitely not buffered), in which fresh  $\text{NO}$  consumes  $\text{O}_3$  and the formed  $\text{NO}_2$  reacts with  $\text{OH}$ . 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”.

Page 11, discussion figure 10. Now it seems that “ $r$ ” is defined as “buffer”, because figure 10 illustrates how  $\text{OH}$  is buffered on the local and global scales. Further the authors write: “the complementarity of the three mechanisms is remarkable”. Is this not the case by definition as “ $r$ ” is being decomposed?

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 ( $\text{O}_3$ ,  $\text{CO}$ ,  $\text{CH}_4$ , 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.

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C6