

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

J. Lelieveld et al.

jos.lelieveld@mpic.de

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This interesting and well written paper describes sources and recycling of OH and HO₂ in the EMAC model. In a few places, I found the text could benefit from clarification, and I think some additions/revisions are needed. A full budget of OH is not presented, and the three ‘OH recycling’ mechanisms are not well defined. I also found it a bit surprising that no comparison with measured values was included. The modelled methane lifetime seems quite short compared to the accepted value – this is a common feature of models, but it goes unmentioned (and I think the comparison with the real world gets worse as more recycling mechanisms are added). Direct comparison to OH/HO₂ measurements is also not evident – we are directed to other papers and the model web-site (p4 I22-23), but these papers seem (from their titles) to evaluate other aspects of the model, not HO_x, and I couldn’t find any mention of the EMAC model version on the

web-site. Some statements in the text appear unsubstantiated or a bit over-blown (see specific comments below). Having said all that, I think if these comments and those listed below are adequately addressed, this paper will make a very useful addition to the literature and should be accepted for publication.

Reply: We will be glad to provide clarifications and additions in the revised manuscript. In the revised manuscript we will present a more comprehensive OH budget and sensitivity simulations to illustrate the impact of the three main OH recycling mechanisms, which will provide a more robust basis for their definition. Comparing with measured OH and HO₂ will be difficult, while an evaluation based on the lifetimes of methyl chloroform and methane will be helpful. In addition, we will include a discussion about measured and modeled OH over boreal and tropical forests, being most relevant in the present context. In the revised manuscript these issues will be discussed more elaborately in relation to previous work. We expect to submit a comprehensive ACP manuscript about the new biogenic VOC chemistry soon (Taraborrelli et al., in preparation), and one on the new anthropogenic aromatics chemistry is under review (Cabrera-Perez, D., Taraborrelli, D., Sander, R., and Pozzer, A.: Global atmospheric budget of simple monocyclic aromatic compounds, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2015-996, in review, 2016.). In the revised manuscript we will update the references.

Specific comments P1 I26 Spivakovsky

Reply: will be changed.

P2 I4 combine, not recombine

Reply: will be changed.

P2 I7 This sentence implies RH features in the previous equation(s), but it doesn't?

Reply: will be reformulated.

P2 I23 I find the definition of 'r' ($= 1 - P/G$) a bit obscure. Isn't $r = S/G$ clearer?

Reply: In our paper of Lelieveld et al (2002) we defined the recycling probability r by solving the differential equation dOH/dt with a Taylor series expansion. We would like to maintain this definition for consistency.

P3 Paragraph from l29 onwards. This paragraph is perhaps not immediately comprehensible to most readers. I suggest you try and make it a bit less technical/more accessible.

Reply: will be done.

P4 l12 ...notably FOR carbon. . .

Reply: will be changed.

P4 l30 ...in SOME previous. . . (Not all previous atmospheric chemistry-transport models have had to artificially reduce natural VOC emissions.)

Reply: will be changed.

P5 l11 may be -> are

Reply: will be changed.

P7 l13 Plane -> Plain

Reply: will be changed.

P7 l25 "...tropospheric production of HO₂ – and thus HO_x. . ." I don't think this follows. Isn't most HO₂ production associated with OH destruction (i.e. HO_x recycling, e.g., R3 and R4)? Production of HO_x is thus only primary production of either OH or HO₂ (i.e. from R1/R2 and HCHO photolysis), whereas production of HO₂ is dominated by conversion of OH to HO₂. Thus production of HO_x and production of HO₂ are quite different.

Reply: good point; will be changed.

P8 l11 Dividing better than 'relating'.

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Reply: will be changed.

P8 I23 I wondered what “strongly underestimated” meant here (it is rather non-specific). I would say normally something that is strongly underestimated is 50% or less of its correct value. From your budget in Figure 6, if the VOC reactions were simplified/not included, I don’t think OH reactivity would be underestimated by as much as 50%. So I think you are being over-dramatic and non-quantitative, which is unhelpful.

Reply: will be changed.

P8 I29 ‘...indicates that air masses that traverse the TTL into the stratosphere have been largely cleansed from compounds that react with OH’. This seems like over-statement – aren’t CO and CH₄ the two main compounds that react with OH in the troposphere? I don’t think TTL air is ‘largely cleansed’ of these two gases?

Reply: Good point; will be changed. We were thinking of compounds that carry halogens into the stratosphere. This will be formulated more explicitly in the revised manuscript.

P8 I30 onwards. The ‘side note’ about SO₂, OH, halocarbons and stratospheric O₃ seems a bit odd.

Reply: Also in view of the critical remarks by ref#1 we will remove this paragraph.

P9 I3 onwards. The discussion of the methane lifetime (to oxidation by OH) of 8.5 years in the model should also be compared to observational estimates (e.g., Prather et al., 2012: 11.2 ± 1.3 yr). Pretty much all models, and EMAC with MOM seems not to be an exception, apparently underestimate the methane lifetime. Do we have any idea why this is? It seems that we need less OH in model’s atmospheres, but by adding new OH sources from recycling this discrepancy gets worse. Doesn’t this suggest that models are missing something fundamental about OH?

Reply: Prather et al. (2012) derive a CH₄ lifetime of 9.10.9 yr, and indicate this is 5% higher than the multi-model mean, as presented in the IPCC (2007) AR4 assessment,

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being 8.71.3 yr. Our estimate is somewhat less (8.5 yr) but still consistent. Prather et al. (2012) relate their CH₄ lifetime to that of methyl chloroform, hence also associated with uncertainty. For example, it is not well known how much methyl chloroform is exchanged with the oceans. Calibrating global OH to a “standard” remains to be a problem, also in view of OH and methyl chloroform distributions. We will probably have to live with some uncertainty, which we nevertheless hope to reduce further in a collaboration project with Wageningen University (Maarten Krol) and NOAA-ESRL (Steve Montzka). We will discuss this issue in greater detail in the revised manuscript.

P9 I31 ‘...over the oceans G is the same as over the continents.’ G is defined earlier (p2 I23) as ‘gross OH formation’. I am unclear whether you mean G over the oceans as a whole compared to G over the continents as a whole, or if you mean per unit area. Obviously this makes a big difference.

Reply: This has been averaged and expresses mean G over the oceans and continents, i.e., per unit area. We will express this more clearly in the revised manuscript.

P10 I7 ‘...S is also the same over the oceans and continents...’ Same query as previous.

Reply: This will also be changed accordingly.

P10 I11 ‘...P declines steeply with solar radiation and water vapor.’ Figure 7 show that P declines steeply with increasing altitude (ignoring the stratosphere) and latitude. Water vapor declines with increasing latitude and altitude (so that’s OK). Solar radiation declines with increasing latitude, but increases with increasing altitude. So the relationship of P with solar radiation seems more complex than stated.

Reply: We will formulate more accurately in the revised manuscript.

P10 I30 ‘is subordinate to’ -> is less than?

Reply: correct.

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P11 I1-2 Isn't 'r' larger in the extra-tropics mainly just because P is small?

Reply: The OH recycling probability would indeed increase if only primary formation would be smaller. However, one expects that primary and secondary OH formation are related and even proportional. The fact that the fraction of secondary relative to primary formation increases with latitude leads to a larger r in the extra-tropics compared to the tropics. This is also the case with altitude. We will formulate this more unambiguously in the revised manuscript.

P11 I2 The last sentence is true for the MBL but not the CBL, so it is incorrect for the BL as a whole.

Reply: Will be corrected.

P11 I4-13 Some clarification of what is exactly meant by the NO_x, O₃ and OVOC 'mechanisms' of OH recycling is needed. The earlier reaction equations and discussion is very good and useful, but I am not completely clear on which reactions make up each mechanism.

Reply: In the revised manuscript we will define the three mechanisms more clearly, also by sensitivity simulations to show what impact they have on OH.

P11 I13 Do you mean from the FT to the BL (rather than 'transport in the FT')?

Reply: Actually it is both, but we agree that in this context "from" is more adequate.

P11 I17 'The complementarity of the three mechanisms is remarkable.' Is it? Don't they have to add up to 100% by definition? Figure 10 is certainly interesting, but I am not sure it is 'remarkable'. As suggested earlier, clearer definitions of the three mechanisms would help the discussion.

Reply: We will delete the word remarkable and more clearly define the three mechanisms in the revised manuscript.

P12 I4 Have you demonstrated in this paper that including MOM 'increases OH reac-

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tivity'? I can believe this is the case, but I don't think you present evidence of what the OH reactivity was in the model before you included MOM.

Reply: We refer to published work, but in the revised manuscript we will discuss the differences in more detail.

P12 I13 I note your reference to 'measurement campaigns'. There is no comparison with observations in this paper, which seems like an oversight. Can you demonstrate that modelled OH is improved and compares well to reality?

Reply: In the revised manuscript we will briefly discuss modeled and measured OH over forested regions (our group has performed and published radical measurements over the boreal and tropical forests), which is most relevant in view of the new MOM mechanism.

P18 Table 1. The caption doesn't adequately describe the table – which contains fluxes for HOx primary production (O1D+H2O), recycling (NO+HO2, O3+HO2, photolysis reactions) and loss (H2O2 deposition). This table could be more comprehensive, and describe the full OH and HO2 budgets, i.e. include all the primary sources, OH to HO2 inter-conversions, and sinks (e.g., Derwent, 1996). The sources and sinks should balance (this is not obvious from the current table). If this were done, it could also clarify the definitions of the three mechanisms, as suggested earlier.

Reply: In the revised manuscript we will adjust the caption and extend the table, as suggested.

P19 Figure 1 (and all zonal mean plots). It looks like surface pressures go up to 1000 hPa everywhere, but that can't be the case over Antarctica (etc.). Is the vertical scale really pressure?

Reply: This is correct. Hence the lower levels over Antarctica in the zonal plots are white. Since we are presenting zonal averages some areas up to 1000 hPa occur almost everywhere, except Antarctica.

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P21 Figure 6. Related to my comments on Table 1 – I note the caption says ‘Main’ production terms of OH. . . Wouldn’t a figure that shows all the OH sources be more useful?

Reply: Considering the comprehensive chemistry scheme in MOM, the figure would become complicated in the VOC part of the pies. This would add little information. The aim of this figure is to provide an overview of the main production terms, i.e., primary formation and the three main OH recycling mechanisms.

P24 Figure 9. The text defines recycling efficiency as $(S-P)/G$. This allows it to take on negative values (where $P>S$). I find this a bit confusing, as efficiency normally refers to a number between 0-100%. The recycling probability (S/G) does just go from 0-100%. I’m not sure you need both quantities?

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

P25 Figure 10. Again, clear definitions of the three mechanisms are needed.

Reply: This will be remedied in the revised manuscript.

References Derwent, R. G. (1996) The Influence of Human Activities on the Distribution of Hydroxyl Radicals in the Troposphere, *Phil. Trans. R. Soc. Lond. A*, 354, 501-531; DOI: 10.1098/rsta.1996.0018 Prather, M. J., C. D. Holmes, and J. Hsu (2012), Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry, *Geophys. Res. Lett.*, 39, L09803, doi:10.1029/2012GL051440

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