

acp-2018-12 authors' response to reviewer 2

Global modelling of the total OH reactivity: investigations on the “missing” OH sink and its atmospheric implications

Reviewers' comments are in black, authors' response in blue and changes to the text in red.

Interactive comment on “Global modelling of the total OH reactivity: investigations on the “missing” OH sink and its atmospheric implications” by Valerio Ferracci et al.

Anonymous Referee #2 Received and published: 1 February 2018

Review of "Global modelling of the total OH reactivity: investigations on the "missing" OH sink and its atmospheric implications" by Valerio Ferracci and colleagues. This is a very interesting study that makes a significant contribution to the field. Increasingly, field experimental campaigns include OH reactivity measurements, which provide an important constraint to our understanding of VOC emissions and their atmospheric oxidation processes. Ferracci et al. introduced a hypothetical sink in their state-of-the-art global atmospheric chemistry transport model to study "missing" OH reactivity, i.e. the reactivity that could not be modelled in comparison to field data. There is one drawback that I would like to see discussed before recommending publication. For the impacts on OH and O₃ in section 4.2 it was assumed that the hypothetical emissions of molecule X, probably representing biogenic VOCs, do not recycle OH through their oxidation products (OVOCs). They are assumed to be a simple OH sink without any further chemistry, which is a rather strong simplification. There is growing evidence that biogenic VOCs are unlikely to be ultimate OH sinks and that OH recycling is ubiquitous. Although mentioned on p. 18 and 20, this aspect needs some discussion in view of the interpretation of atmospheric chemistry impacts, notably in the abstract and conclusion section.

We thank the reviewer for their kind words on the manuscript and for their valuable feedback. We understand that the absence of OH recycling constitutes a limitation of this study. However, as also explained at the beginning of Section 4.2, we feel that there are too few constraints to even attempt modelling of OH recycling following reaction 3. In the most optimistic view, it would involve running different recycling scenarios, with each scenario requiring to re-run the iterative routine to determine the emissions of X as the recycling of OH would ultimately

perturb steady state $[X]$ and ultimately $k_3[X]$, *i.e.* the modelled missing reactivity. We conclude that the work described in the manuscript provides an upper limit on the effects of the missing reactivity on the oxidising capacity of the atmosphere. We have added a statement to address this in both the abstract and conclusions.

“As no OH recycling was introduced following the initial oxidation of X, these results can be interpreted as an upper limit of the effects of the missing reactivity on the oxidative capacity of the troposphere.” and “It has to be noted that, as no OH recycling was introduced following the initial oxidation of X, these results should be interpreted as an upper limit of the effects of the missing reactivity on the oxidative capacity of the troposphere.”

Other than that, I recommend publication in ACP with minor revisions.

Minor comments:

-Please define missing reactivity more clearly. Is it missing in the sense that accompanying VOC measurements do not account for all reactivity, or missing in the model. Please make the distinction.

We have added a clearer definition of missing reactivity after Figure 2 in Section 3.

“The total observed k_{OH} in Figure 2 is made up of contributions from the measured OH sinks, from modelled intermediates (only available for some of the field campaigns presented here) and from reactivity that is unaccounted for by known OH sinks, *i.e.* the missing reactivity. “

-p10 bottom/p.11 top: It would be helpful to compare the model calculated OH with some of the published OH measurements in the Amazon. Often, isoprene chemistry mechanisms severely underestimate OH.

The reviewer makes a very valid point. The OH measurements from Liu et al. (Liu et al., *PNAS* 2016) and from the GABRIEL campaign (Martinez et al., *Atm. Chem. Phys.*, 2010) were compared with the model output. It has to be noted that Liu et al. only measured OH for ~7 hours on a single day, and that the GABRIEL campaign in Suriname consisted of airborne measurements. The model underestimated OH by almost a factor of 4 in both cases, indicating that there is a strong possibility that the high concentrations of modelled VOCs for the ATTO site are caused by underpredicted OH. This is consistent with the inverse relationship between OH reactivity and OH concentrations as shown in Figure R1 below.

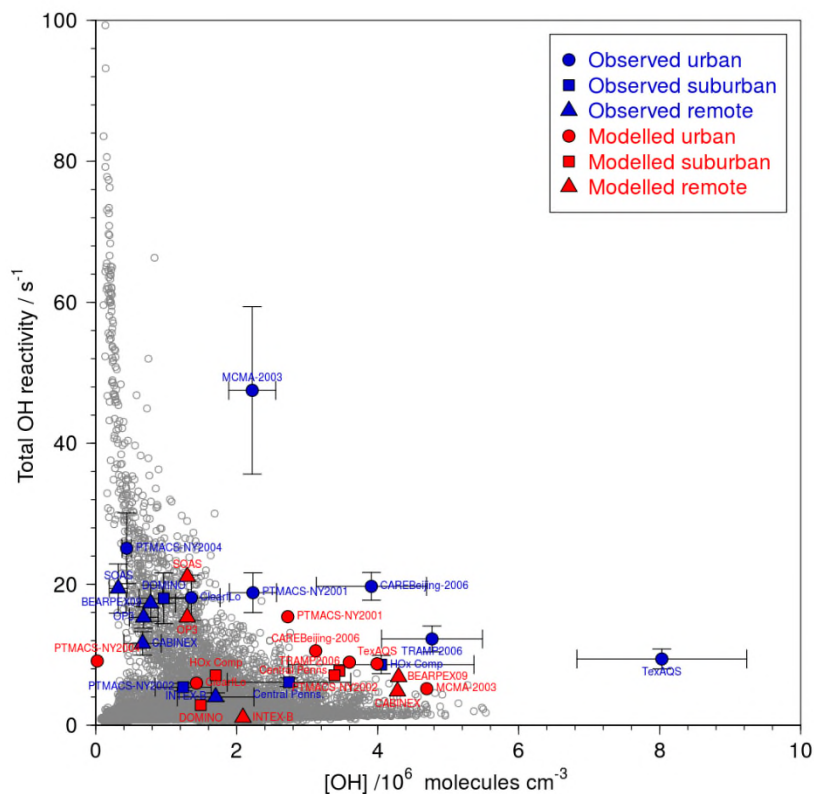


Figure R1: Scatter plot of total OH reactivity against OH concentration. Observations from field studies (in blue) and values from the UM-UKCA model for the same locations (in red) are shown. Also shown is the model output for the surface (grey points) to highlight the inverse relationship between k_{OH} and $[OH]$.

The text has been modified to account for this.

“Figure 3 also offers an explanation for the instances in which the model significantly over predicted k_{OH} . For example, the abundance of isoprene measured during the wet season of the ATTO campaign in the Amazon ($\sim 1 \pm 0.1$ ppbv, or nmol/mol, in March 2013) was more than an order of magnitude lower than that predicted by the model for the same time of the year (~ 14.6 ppbv). As discussed above, this might arise from either overestimated isoprene emissions or from underestimated OH abundances in the model. As OH concentrations were not measured during the ATTO campaign, a direct comparison of modelled and observed $[OH]$ is not possible. However $[OH]$ measurements from campaigns carried out in neighbouring parts of the Amazon (Liu et al., 2016) and in the Suriname rainforest (Martinez et al., 2010) might help address this point. Indeed the model underestimates $[OH]$ by almost a factor of four on average in both cases, although it is worth noting that $[OH]$ measurements from Liu et al. (2016) only cover ~ 7 hours on a single day, while the GABRIEL campaign in Suriname consisted of airborne measurements, and only the OH data for the boundary layer were considered for comparison with the model. It may also be indicative of underrepresented $[OH]$

in model that the abundance of other short-lived OH sinks in the ATTO campaign is also overestimated by the model; notably, the observed concentration of monoterpenes (reported to be below the detection limit of the PTR-MS used by Nölscher and co-workers, and here approximated to 0.01 ppbv) was much lower than in the model (2.2 ppbv). Underrepresented OH in the model might arise from underestimating the secondary OH originating from the oxidation of large organics (e.g., isoprene and monoterpenes, as described in Archibald et al., 2010). In this specific instance the model also underestimated the concentration of NO (34 pptv, or pmol/mol, vs the observed $\sim 1 \pm 0.05$ ppbv), which might have limited the production of secondary OH via the reaction of HO₂ with NO relative to observations.”