acp-2018-12 authors' response to reviewer 1

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. <u>Anonymous Referee #1</u> Received and published: 6 February 2018

This paper presents a study of the global impacts of "missing OH reactivity" in models used to determine the atmospheric oxidising capacity, and investigates the extent to which additional sinks are required to reconcile observations of OH reactivity with model simulations. The authors use an interesting approach to determine the emissions field necessary to improve the agreement between observed and modelled OH reactivity. The impacts of the reaction between OH and CH_3O_2, and its branching ratio, on budgets for OH, CH_3O_2 and the global methane lifetime are also discussed.

In general, the paper is well written and will be of interest to the atmospheric science community. However, the discussion would benefit from some additional detail regarding the regions and environments affected most by missing reactivity, and how the OH and HO_2 concentrations are affected in the model.

We would like to thank the referee for their support of our paper and for their constructive comments. Below are the answer to the reviewer's comments, point by point.

We feel that the regions affected by measured missing reactivity are already described at length in the introduction (where observations of missing reactivity are discussed) and in Section 4.1, where the geographical distribution of the modelled missing reactivity from multiple linear regression is described. We have added a sentence in the conclusions discussing the regions and environments where the multiple linear regression predicts the presence of missing reactivity.

"The multiple linear regression indicated that the areas most affected by the missing reactivity would be tropical remote regions, where biogenic emission dominate, as well as urban regions all over the globe, where anthropogenic emissions are significant. This result agrees with the type of environments in which missing reactivity has been observed."

Effects of X + OH on OH are already shown in Fig 7 and Figs S2 and S3 (now Figures S8 and S9 in the revised manuscript) and discussed in detail in the text. An additional figure (Figure S10) has been included in the Supplementary Information showing that relative changes in HO_2 from X + OH largely mirror those in OH, albeit with a somewhat reduced relative magnitude. Changes in OH and HO_2 abundances from CH_3O_2 + OH are already discussed at length in Section 5.2.

The results of this work could also be used to provide some recommendations as to where future measurements of OH reactivity are most needed to give better constraint for modelling of global methane lifetimes and ozone budgets.

The Southern Hemisphere was notably underrepresented in the sample of measurements analysed in this study. Aircraft measurements of the missing reactivity would also be desirable, especially at tropical and mid-latitude, to better quantify the impact on global methane lifetimes as well as the vertical profile of the missing reactivity, especially above the boundary layer. A comment to address these points was added to the Conclusions.

"Lastly, as observations of the missing reactivity so far are largely limited to ground level measurements in the Northern Hemisphere, further observations in the Southern Hemisphere as well as aircraft measurements both in the boundary layer and the free troposphere would provide additional constraints to the modelled oxidising capacity of the atmosphere."

Minor comments are listed below.

Page 2, line 6: $O(^1D)$ production is observed at wavelengths below 340 nm.

Amended.

Page 3, line 5: Please comment on the location for which 80 % of the total k_{OH} is missing.

Some text was added in the first two paragraphs on page 3 to indicate that the measurements of up to 80% missing reactivity took place in the Amazon, where the impact of large

unidentified biogenic emissions as well as the complex oxidation chemistry of measured and unmeasured BVOCs is largest.

Page 4, line 23: Please update the reference to http://iupac.pole-ether.fr/

Amended.

Page 7-8, Table 2: Does the use of the mean k_{OH} measured over the whole duration of each campaign skew the averages in any way? Do all the field campaigns have similar data coverage throughout the day or throughout the campaign?

There are a number of campaigns with discontinuous temporal coverage that were not included in the analysis presented in the manuscript. These include 4 sets of measurements in Tokyo, Japan, which only reported daytime values of the OH reactivity (Yoshino et al., *Atm. Env.*, 2006; Chatani et al., *Atm. Chem. Phys.*, 2006; Kato et al., *Atm. Env.*, 2011; Yoshino et al., *Atm. Env.*, 2012). Similarly, measurements in Suriname (Sinha et al., *Atm. Chem. Phys.*, 2008) were discarded as they only covered a limited interval of time on a single day.

We believe that, whilst there is always a possibility that the measurement temporal coverage in a field campaign is not uniform or continuous, the choice of campaigns that spanned many weeks (which was the case for the vast majority of the datasets considered for the missing reactivity calculations) does at least minimise that risk.

Page 8, Figure 2: Is there a reference for the 20 % measurement uncertainty in observed k_{OH}? I would expect this to depend on the specific technique used to measure k_{OH} and the particular instrument configuration.

The reviewer is correct and the error bars in Figure 2 (and Figure 4) have been amended to reflect the different uncertainties of the instruments used in each campaign.

Page 10, line 1: Please quantify, or avoid, the statement 'reasonably good agreement'.

The line has been changed to better quantify the agreement between model and observations in Figure 3.

"Overall more than half (53 %) of the reactivities calculated from modelled sinks agree with observations within a factor of two, and the vast majority (88 %) within a factor of ten."

Page 17, Figure 6: How many iterations are typically required to obtain the emissions field? Is the R^2 in the lower panel of Figure 6b skewed by the few points with high reactivity?

The work described in the manuscript involved 10 iterations of the routine described in figure 6.

Exclusion of the points with highest reactivity (> 50 s^{-1}) from the fit in the lower panel of Figure 6b still returns an R^2 value > 0.95 (0.9515 to be precise, *cf.* 0.9588 obtained with the full dataset). It is necessary to remove all points of reactivity higher than 40 s^{-1} to get an R^2 value < 0.95 (0.9489). It has to be noted that we use 0.95 as an arbitrary threshold for the R^2 value. Moreover, progressive removal of points of high reactivity indicates that these high values are not skewing the R^2 value significantly: a fit considering only values lower than 30 s^{-1} still returns an R^2 of 0.943 (a very modest 1.6% decrease compared to the full data set).