

## acp-2018-12 authors' response to reviewer 3

### 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 #3 Received and published: 1 February 2018

The article entitled “Global modelling of the total OH reactivity: investigations on the “missing” OH sink and its atmospheric implications” concerns first the modelling of the OH reactivity at the global scale with the model UM-UKCA (base case) and the comparison with measured total OH reactivity in various environments (27 field measurement used for the comparison). The model reproduces well the measured OH reactivity (within 20%) for 12 campaigns, underestimate it for 14 cases and overestimate it for one case. An individual analysis of the differences between the modelled and calculated reactivity per species reacting with OH on 11 categories highlights the main source of underestimation by the model: the NMHCs whereas the overestimation case is due to the isoprene concentration overestimation. This work is of high interest because there are only a few studies on the oxidant capacity of the atmosphere with global atmospheric modelling and this study is the first one dedicated to the comparison between measured and modelled OH reactivity.

In a second step, an original approach has been used to represent at the global scale the missing reactivity through the addition of a hypothetical molecule X, reacting with OH (but without OH recycling), at various concentrations depending on the missing reactivity measured in the different campaigns. The emission rate of this species has been determined by a multiple linear regression including 15 categories of emission and an iterative procedure to match the missing reactivity observed. The impact of this addition is analysed through the depletion of OH concentration (up to 90% in the eastern Europe for example), the methane and OH lifetime (respectively 2.3 and -2% at the surface) and the ozone change has been used to quantify the impact of this missing reactivity on the OH lifetime at the global scale as well as the impact on the tropospheric methane lifetime in comparison to the base case. This approach allows to

represent the missing reactivity at a global scale but the absence of OH recycling due to this species is a limitation to analyse further the consequence of the missing chemistry highlighted by the missing reactivity measured.

In a third step, the UM-UKCA model has been used to study the impact of the reactions of peroxy radicals with OH on OH reactivity which was found to be weak (maximum of  $0.12 \text{ s}^{-1}$ ) and can't be the reason for the missing OH reactivity. In the last part of the article, the impact of the products yields of the reaction of  $\text{CH}_3\text{O}_2 + \text{OH}$  has been studied with 3 extra model runs with different branching ratio for the different product channels (producing respectively HO2 or methanol). The branching ratio has been varied for these 2 channels between 1/0 and 0.6/0.4. The conclusion of this work is that, even with the highest branching ratio used for the channel producing methanol (0.4), the additional production of methanol does not explain the under-prediction of methanol by the models. Even if of high interest, this part seems to be decoupled from the other parts of the article dedicated to the OH reactivity. The article is very interesting and the method and the analysis done on the reactivity based on the comparison between measured reactivity and modelled one is well structured. However, I found sometimes difficult to find the information and some improvements in the Figures could help the reader.

We thank the referee for their kind support of the manuscript and for their constructive comments. Below are the answer to the reviewer's comments.

Comments:

(1) P7: would be interesting to add in Table 2 the total modelled  $k_{\text{OH}}$  per campaign to identify better the cases described p9 and quantify the under or overestimation mentioned P9 L2-3. A graph with the reactivity modelled vs reactivity calculated and measured would be useful (in the SI?). For example, for the 14 cases with an OH reactivity underestimated significantly by the model, does it correspond to similar missing reactivity with the calculated reactivity?

An additional column for the total modelled  $k_{\text{OH}}$  was added to Table 2.

Plots of modelled reactivity vs observed and calculated reactivity were added in the Supplementary Material. Generally, the modelled reactivity is in better agreement with the calculated reactivity than the observed reactivity, even though the model still underestimates the calculated reactivity in urban and suburban environments. This can be mainly accounted for in terms of the reactivity arising from NMHCs, as explained in the text.

As Figure 2 was changed to address the following comment, the discussion on the agreement between modelled and observed reactivity was amended to reflect the new information provided by the new version of Figure 2.

(2) P8: similarly, in Figure 2, it would be useful to add the calculated reactivity including the contribution of the species used in Figure 3 for the calculated and the modelled reactivity. Even if the information is redundant with the Figure 3, the different presentation will help to better identify the different types of environments. The uncertainty varies from one instrument to another one and the same one is used here and in the whole document, please justify this choice.

We changed Figure 2 to show the calculated reactivity from measured species as well as the reactivity from reaction intermediates (when available) and the missing reactivity. We have also included a version of Figure 2 with the speciation of the reactivity (hence incorporating the information in Figure 3) in the Supplementary Material as Figure S5. As the reviewer suggested, this figure offers an effective way to distinguish the different environments: urban sites are dominated by NO<sub>x</sub> and NMHCs; remote sites by biogenic VOCs (mainly isoprene and its oxidation products), with suburban environments sitting somewhere in between the previous two. The text between Figures 2 and 3 (as well as the caption of Figure 2) has been amended to reflect this change.

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

(3) A short discussion on the different techniques used to measure the OH reactivity and the potential impact on the measurements in the different campaigns should be added.

We have added some additional text on page 2 to describe the main techniques used to measure  $k_{OH}$  in the field, however we feel that a too detailed account would detract from the main objectives of the manuscript. The reader is referred to two recent works (Yang et al., 2016 and Fuchs et al., 2017) in which the experimental techniques are extensively reviewed.

(4) P9, Figure 3: the title used for the x axis is not appropriate and confusing, I would change it for “calculated reactivity from measured species”

Amended (the y-axis label was also amended).

(5) P10, it is mentioned that “it is difficult to establish whether the differences between observed and modelled OH sinks arise from misrepresenting emissions or abundances of the hydroxyl radical itself without comparing modelled and observed [OH], and measurements of the OH concentrations are only available for a small subset of the campaigns considered here.” From these campaigns, at least, wouldn't it be possible to provide a “most probable” reason for the difference?

A correlation plot of modelled vs observed [OH] was added in the Supplementary Material for those campaigns that measured OH as well as the total reactivity and the individual OH sinks. In a couple of cases in which the model overestimated [OH] by roughly a factor of six (BEARPEX09 and CABINEX), the modelled isoprene concentrations were approximately a factor of two lower than the observations in both cases. There are no OH measurements available for the campaigns that exhibited the largest disagreement between observations and model (namely, ATTO), but analysis of OH measurements in Amazonia from different campaigns (see response to reviewer 2) indicate that the model might underrepresent OH in these locations, hence resulting in higher isoprene and VOCs than in the observations. This behaviour is illustrated in Figure R1 in the response to reviewer 2. The text on pages 10-12 has been amended accordingly.

“A correlation plot of modelled against observed [OH] is given in the Supplementary Material (Figure S6) for those campaigns that measured OH as well as the total reactivity and the individual OH sinks. In a couple of cases in which the model overestimated [OH] by roughly a factor of six (BEARPEX09 and CABINEX), the modelled isoprene concentrations were approximately a factor of two lower than the observations in both cases.”

(6) P11 L8: the difference between modelled and measured NO concentration should be modulated considering the uncertainty and the LOD of the instrument.

The NO instrument used for the ATTO measurements (Ecophysics chemiluminescence analyser, model CLDTR-780) has a LOD = 0.05 ppb and uncertainty < 5% (as reported by Williams et al., *Atm. Env.*, 2016). Even in the light of the measurement uncertainty, the observed [NO] is considerably larger than in the model. We have added the measurement uncertainty to the text for clarity. We have also added the uncertainty in the isoprene measurement (as reported by Yanez-Serrano et al., *Atm. Chem. Phys.*, 2015) at the beginning of the same paragraph.

(7) P11 L22: even if the use of additional species and their intermediates provided different results with most of the time a remaining missing reactivity, it would be interesting to see at the global scale the effect of considering that in complement to the use of X which has the disadvantage of being a unique species, with a unique behavior at the global scale.

This approach, while feasible for box models used to interpret the results of the individual field campaigns, would be extremely burdensome for a global model like UM-UKCA. It is still an interesting area, worth investigating in future studies.

(8) P15: the Figure 5 shows simulated missing reactivity up to  $100 \text{ s}^{-1}$ , which is a lot higher than the highest one observed. Could it be commented (due to the model or to the measurement, also based on the potential underestimation of the OH reactivity in specific environments)?

The vast majority of the missing reactivity values plotted in Figure 5 are below  $10 \text{ s}^{-1}$  (87% of all non-zero entries), and the near totality are below  $50 \text{ s}^{-1}$  (99.8%).

Values of the missing reactivity higher than  $50 \text{ s}^{-1}$  are only found in 12 grid cells over the whole globe in DJF and in 15 grid cells JJA in Figure 5. Upon closer inspection, these correspond to areas of high anthropogenic emissions (principally large urban areas), listed in the table below for the JJA plot in Figure 5. For the majority of these entries the missing reactivity is dominated by large contributions from the highly-correlated organic and black carbon emissions from biofuels (OC and BC biofuel emissions in Table 3 in the manuscript). However in a small number of cases (Caracas, Dubai, Kuwait City) the missing reactivity appears dominated by emissions related to the oil refinery industry (propane, formaldehyde).

Longitude / ° E	Latitude / ° N	Location	Missing reactivity from MLR / $\text{s}^{-1}$
112.5	-7.5	Surabaya (East Java), Indonesia	50.65
106.875	-6.25	Jakarta, Indonesia	60.61
292.5	10	Caracas, Venezuela	58.27
292.5	11.25	Caracas, Venezuela	56.21
106.875	21.25	Hanoi, Vietnam	56.37
90	23.75	Dhaka, Bangladesh	81.36
56.25	25	Dubai, UEA	94.30
90	25	Brahmaputra river, Bangladesh	67.12
48.75	28.75	Kuwait City, Kuwait	66.17
48.75	30	Kuwait/Iraq/Iran border, North Persian Gulf	85.46
69.375	41.25	Tashkent, Uzbekistan	60.37
26.25	45	Bucharest, Romania	62.71
28.125	47.5	Chisinau, Moldova	56.93

37.5	56.25	Moscow, Russia	99.99
30	60	St Petersburg, Russia	91.78

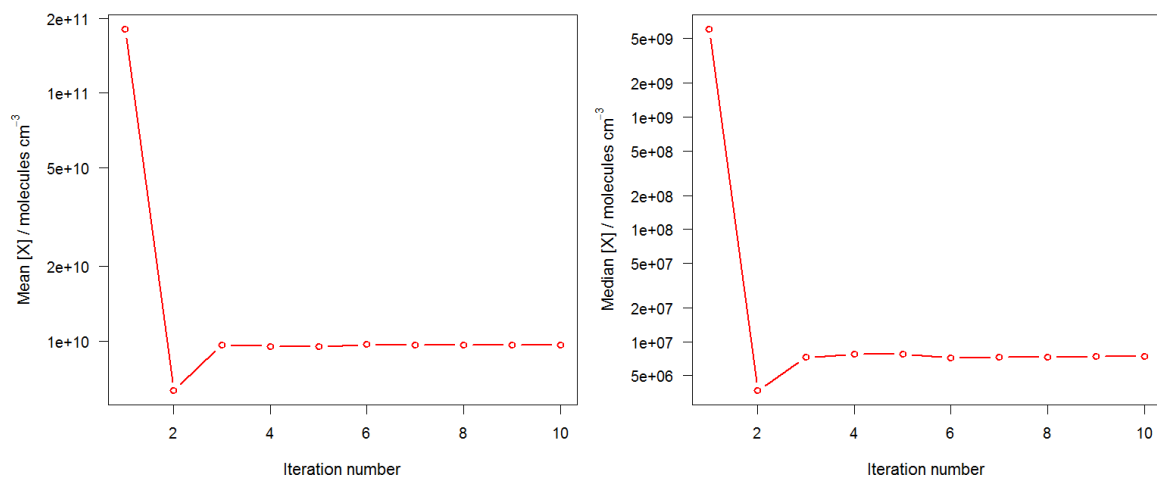
We believe these high values are ultimately a result of the MLR approach used in this work. A paragraph describing the distribution and magnitude of the modelled missing reactivity across the globe has been added to Section 4.1 (after Figure 4 and before Table 3).

“Overall, the modelled missing reactivity obtained from the multiple linear regression had values other than zero in 23 % of the surface grid cells in DJF and in 32 % of the grid cells in JJA. Of all the non-zero values plotted in Figure 5, 57 % are below  $1 \text{ s}^{-1}$ , 77 % below  $5 \text{ s}^{-1}$ , 87 % are below  $10 \text{ s}^{-1}$  and 99.8 % are below  $50 \text{ s}^{-1}$ . Only a very small number of grid cells have modelled missing reactivities in the range  $50\text{-}100 \text{ s}^{-1}$  (12 grid cells in DJF and 15 in JJA). These regions correspond to areas of high anthropogenic emissions that resulted in large contributions of the strongest predictors (OC and BC biofuels) to the calculated missing reactivity.”

(9) P16: I do not understand why the OH reactivity calculated at the first step of the iteration is so overestimated. What can be the assumption(s) done on the calculation of the emission rate of X which could explain this disagreement? How does evolve the concentration of X between the first and the last run?

We believe that the large overestimate in OH reactivity due to X after the first step in the iteration is due to the values of [OH] used in Eq. (2). As stated in the text, the [OH] field is taken from the base run (*i.e.*, in the absence of X). As the introduction of an additional OH sink perturbs the OH field itself (leading to lower OH abundances), the OH field from the base run is itself an overestimate of the OH abundances found when X and OH are in steady state. A sentence describing this was added to the manuscript.

Overall the concentration of X decreases between the first and the last run as shown in Figure R2 below (mean and median [X]). The first iteration shows a very large overestimate, for the reasons described above. The second iteration somewhat over-corrects for the first one and the subsequent ones give more or less a steady mean/median values of [X].



**Figure R2:** Variation of mean (left) and median (right) [X] as a function of iteration number.

(10) P17, L17: wouldn't it be possible to have different runs including different OH recycling to test its influence?

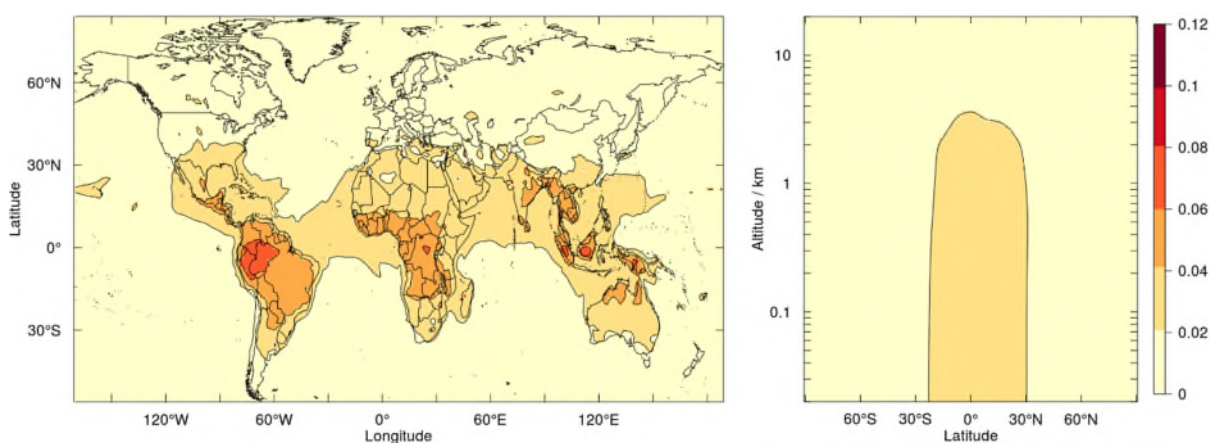
As we mentioned in our reply to Reviewer 2, introducing different OH recycling would involve running the iterative routine to determine the emissions of X in each scenario, as the recycling of OH would ultimately perturb steady state [X] and ultimately  $k_3[X]$ , *i.e.* the modelled missing reactivity. We prefer presenting the work described in the manuscript as an upper limit of the effects of the missing reactivity on the oxidising capacity of the atmosphere. As requested by Reviewer 2, we have re-iterated this in both the abstract and conclusions.

(11) P21: It is not clear in the article what is considered to study the impact of the reaction  $RO_2 + OH$  on the OH reactivity, first and second generation peroxy radicals produced in the oxidation of isoprene are mentioned but what about the other products and the products of these reactions? Could you clarify this point? It would be useful also to provide (in the SI?) a map of the  $RO_2$  and also  $HO_2$  concentrations. As the reaction of  $HO_2 + OH$  is as fast as the  $RO_2 + OH$ , could you specify if this reaction has been added in the reactivity?

A clearer list of the peroxy radicals included in the model was added to the first paragraph of Section 5.1. We have also specified more clearly that the contribution of all  $RO_2$  radicals to the total  $k_{OH}$  was calculated offline, so that the individual  $RO_2 + OH$  reactions were not added to the model, as this would require some degree of knowledge of their products. The one exception is of course the reaction of methyl peroxy + OH, which is described in Section 5.2.

Maps of HO<sub>2</sub> and total RO<sub>2</sub> concentrations were added to the Supplementary Material as Figures S2 and S3 respectively..

The HO<sub>2</sub> + OH reaction was included in the main reactivity calculations described in Section 3 of the manuscript. The magnitude of this term is smaller than that calculated for the total RO<sub>2</sub>, as shown below in Figure R3 (in s<sup>-1</sup>, using the same scale as Figure 10a and 10b).



**Figure R3:** Annual mean reactivity from the HO<sub>2</sub> + OH reaction in s<sup>-1</sup>.

(12) P23: as mentioned previously, even if of high interest, the last part of the article, on the impact of the branching ratios for the reaction CH<sub>3</sub>O<sub>2</sub> + OH seems to be decoupled from the other parts of the article dedicated to OH reactivity. Indeed, the aim of this study is to determine the impact of the reaction on the HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub> and methanol concentrations but without further analysis on the OH reactivity. A part dedicated to the RO<sub>2</sub> + OH and the impact of their products on the reactivity, including the different RO<sub>2</sub> would fit better in the article than the part only based on the change in the concentration of the products of CH<sub>3</sub>O<sub>2</sub> + OH.

A paragraph was added at the end of Section 5.2 to better address how the chemistry of CH<sub>3</sub>O<sub>2</sub> + OH fits within with the wider theme of OH reactivity; figures have also been added in the Supplementary Material to illustrate the changes in  $k_{OH}$  brought about by R4 (Figures S13 and S14).

“As the species affected by R4 (HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>OH) are all OH sinks, changes in their concentrations are accompanied by changes in  $k_{OH}$ . However these are modest ( $< 0.25 \text{ s}^{-1}$ ) in all the scenarios considered in this work, as shown in Figures S13 and S14 in the Supplementary Material. While the reactions of OH with both HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> have large rate constants ( $> 1 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ), the general low abundance of these species (of the



order of  $\sim 10^8$  molecules  $\text{cm}^{-3}$ , as shown in Figures S2 and S3) results in small changes to the total  $k_{\text{OH}}$ . On the other hand, while some of the changes in methanol concentrations arising from R4 are significant (with increases up to 400 pptv in run 3, corresponding to  $\sim 1 \times 10^{10}$  molecules  $\text{cm}^{-3}$ ), the very small rate constant of its reaction with OH ( $< 1 \times 10^{-12}$   $\text{cm}^3$  molecules $^{-1}$  s $^{-1}$ ) leads to a small contributions to  $k_{\text{OH}}$ . These results are consistent with the magnitude of the changes in  $k_{\text{OH}}$  calculated offline for all RO<sub>2</sub> radicals in Section 5.1. It remains to be seen if any of the reaction products of more complex RO<sub>2</sub> radicals with OH, or their combination, might have a significant impact on  $k_{\text{OH}}$ .”

(13) P25: the change in methanol concentration is only provided in the text whereas it is the main result of this section. It would be useful to provide a figure similar to Figure 11 and 12 but for methanol and for the 3 runs. It would be useful to write in the Legend of Figure 11 and 12 the corresponding run.

Agreed. A figure showing the changes in methanol under the three scenario was added (Figure 13).

The corresponding run for both Figures 11 and 12 was added to the captions.

(14) P25: the conclusion that the branching ratio needed for this channel (0.8) is not possible seems too extreme because the branching ratio for channel 1 (producing HO<sub>2</sub>) has been determined only at low pressure.

Agreed. As theoretical studies seem to indicate the presence of a termolecular association channel (Müller et al., *Nat. Commun.*, 2016; but also Liu et al., *Chem. Res. Chin. Univ.*, 2017 for ethyl peroxy + OH) leading to the formation of CH<sub>3</sub>OOOH (which could potentially decompose to CH<sub>3</sub>OH and O<sub>2</sub>), we have added a sentence to highlight the need for further characterisation of the branching at ambient pressure.

“However it has to be noted that so far the product branching of R4 has only been measured at low pressure (50 Torr) by Assaf et al. (2017b). Calculations by Müller et al. (2016) suggest the presence of an association channel leading to the formation of a trioxide (CH<sub>3</sub>OOOH) species, which might potentially decompose to methanol and molecular oxygen. As the stabilisation of association products is generally a pressure-dependent process, it is very important that future studies address the branching of R4 at ambient pressure.”