

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

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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

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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 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 CH₃O₂+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 underprediction 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.

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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.

Comments:

(1) P7: would be interesting to add in Table 2 the total modelled kOH 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? (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. (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. (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" (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? (6) P11 L 8: the difference between modelled and measured NO concentration should be modulated considering the uncertainty and the LOD of the instrument. (7) P11 L22: even if the use of additional species and their intermediates

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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. (8) P15: the Figure 5 shows simulated missing reactivity up to 100 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)? (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? (10) P17, L17: wouldn't it be possible to have different runs including different OH recycling to test its influence? (11) P21: It is not clear in the article what is considered to study the impact of the reaction RO₂+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 RO₂ and also HO₂ concentrations. As the reaction of HO₂+OH is as fast as the RO₂+OH, could you specify if this reaction has been added in the reactivity? (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 CH₃O₂+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 HO₂, CH₃O₂ and methanol concentrations but without further analysis on the OH reactivity. A part dedicated to the RO₂+OH and the impact of their products on the reactivity, including the different RO₂ would fit better in the article than the part only based on the change in the concentration of the products of CH₃O₂+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. (14) P25:

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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 HO₂) has been determined only at low pressure.

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