

## ***Interactive comment on “Parameterisation and impact of aerosol uptake of HO<sub>2</sub> on a global tropospheric model” by H. L. Macintyre and M. J. Evans***

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The authors wish to thank the referees for their useful comments on the paper. Issues raised by referee #1 are addressed first, with points from referee #2 addressed second. Finally we address comments made by Dr Russel Saunders.

### **Comments from referee #1.**

#### **1) Technical corrections.**

C9855

p.16315, line 11: “*such \*as\* sulfate*”. Changed accordingly.

p.16320, line 22: *I think “using” is missing from “...simultaneously {} the lower”...*  
Changed accordingly.

Table 2: *Over what altitude ranges are the burdens calculated?*. These are tropospheric burdens, figure caption changed.

Fig. 3: *Clarify in the caption that you are showing the ratio of the 2 results*. Clarified accordingly.

### **Comments from referee #2.**

#### **1) Justification for the parameterisation.**

Referee #1 comment: “...given (1) the very large uncertainty in the HO<sub>2</sub> reaction mechanism, (2) the large divergence in measured reaction probabilities over a very limited range of atmospheric conditions, (3) large uncertainties about the actual composition, pH, and phase state of tropospheric aerosols, the value of a parameterisation based on a very small number of highly idealized laboratory systems is highly questionable. The authors need to justify such a parameterisation in light of the above issues.”

We agree with the reviewer that there are significant uncertainties in the reactive uptake coefficients. Despite the uncertainties, we believe that there is value in representing our current state of understanding in a model. We have added the following sentences to the introduction, discussion, and conclusion sections to emphasise the uncertainties and the impacts.

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(At line 20, p 16315): “Previous parameterisations of HO<sub>2</sub> uptake by aerosols have been based on gross simplifications (all aerosol types have the same value of gamma under all temperature and relative humidity conditions) or upon the assumption that the underlying chemistry for the uptake is based on our limited understanding of aqueous phase chemistry. In this work we develop a new parameterisation based on the available but limited laboratory data. We then explore the impact of assumptions about the reaction products on global composition.”

## 2) Comparison with other parameterisations.

Referee #1 comment: “... My second concern is that this new parameterisation results in different reaction probabilities but not different impacts compared to the Thornton 2008 parameterisation that the authors also used for comparison. See for example Tables 2 and 3. And yet, even though the impacts of the two parameterisations are essentially identical relative to a situation where the reaction probability is set to a constant value, the authors seem to focus on the differences in the reaction probabilities and do not even mention as far as I can tell how similar the two parameterisations are in terms of impacts. Ultimately, isn't the interest in the effect of the parameterisation on other atmospheric constituents? A revised version should focus on the similarities between the two parameterisations and the reasons for the similarities even though the reaction probabilities are different.”

The reviewer makes a good point. We have updated the text to reflect the similar impact of the different parameterisations, and the reasons for this. We have also included a figure of the reaction rates.

(At line 14, p 16319):

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“Although differing values for  $\gamma_{\text{HO}_2}$  are calculated using the scheme presented here compared with that of Thornton et al. (2008) (Figure 4), the resulting changes in global burdens are rather similar (Table 2). Figure 6 shows the annual zonal mean heterogeneous reaction rates calculated using the parameterisation in this work and that used by Thornton et al. (2008). At the surface, the extra-tropics give very similar rates with larger differences at the tropics. There are significant difference in the upper troposphere which reflect the differences in the temperature dependencies of the two parameterisations. Given much of the mass of the atmosphere lies within the lowest 5 km, the impact of the the differences in the upper troposphere on the global impact is relatively small. “

## Detailed comments.

### 3) Lower limits.

Referee #1 comment: “The authors conclude their parameterisation is likely a “lower limit”, however, that is only true for the small ranges that have been probed in the laboratory, and even then I would argue it is only strictly true that all laboratory measurements lead to reaction probabilities biased low. For example, using high HO<sub>2</sub> concentrations can potentially bias the loss rate high due to self-reaction.”

Our meaning for the phrase ‘lower limit’ has not been clear in the text. We refer to ‘lower limit’ to indicate that we have not taken into account the potential impact of transition metals (notably Cu(II)) on our calculation. We have updated the text to reflect our meaning for the term.

We have added a couple of sentences about this into the paper:

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(At line 10, p 16316): "As the potential impact of transition metal catalysis is not considered in the parameterisation presented here, this likely represents a lower limit."  
(At line 2, p 16322): "This work uses measured rates from available laboratory studies to avoid the overestimates that may have been made previously, thus the parameterisation likely represents a lower limit as we neglect the potential impact of transition metal catalysis."

#### **4) Show actual data used for the parameterisation.**

Referee #1 comment: *"Would it be possible to show the actual data used to make the parameterisation? At the moment I wouldn't call what is described in the manuscript a "review" of laboratory data."*

We have added a figure in here which summarises available laboratory data and parameterisations. (At line 14, page 16315): "Available laboratory studies and parameterisations of  $\gamma_{\text{HO}_2}$  are summarised in Figure 1."

#### **5) Differences in rate, not gamma.**

Referee #1 comment: *"A direct comparison of reaction probabilities from the two parameterisations is not all that instructive because what is actually of interest is the heterogeneous reaction rate, which is a function primarily of the reaction probability, particle size, and particle surface area concentration. Given the non-linear dependence of the heterogeneous reaction rate on reaction probability that arises due to the gas-phase diffusion limitation, a much higher reaction probability doesn't necessarily translate into a much higher heterogeneous loss rate. However, the authors do not mention this aspect in the text and instead only highlight the differences*

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*in reaction probability. This issue is at least partly the explanation for why, even though reaction probabilities between the two parameterisations differ, the actual impacts do not. Thus, a figure that compares the heterogeneous reaction rate would be more informative as a direct comparison. A second reason for the lack of sensitivity between the two formulations is that the heterogeneous reaction rate just isn't all that important as a HOx sink in the regions where the reaction probabilities differ the most."*

We agree with the reviewer with these points. We have amended the text and included a plot of the overall rate of uptake (rather than  $\gamma_{\text{HO}_2}$ ) in the paper (see response to issue 2 above).

#### **6) Reaction limitations.**

Referee #1 comment: *"Pg 16318, line 9. Aren't the laboratory measurements lower limits (as mentioned earlier) due to strong diffusion limitations in the experiments? I would think the Thornton 2008 parameterisation, if it depends upon aqueous phase chemistry, would depend upon pH and thus for a truly consistent comparison the pH of sulfuric acid droplets (if that is truly a correct assumption about upper tropospheric aerosol) would have to be used."*

We again apologise for our terminology here. The term 'lower limit' here refers to the lack of transition metal catalysis in the model calculations. We have updated the text to clarify this (see response to issue 3).

**Comments from R. Saunders.**

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“p 16313, line 7 - gamma spans several orders of magnitude ( $< 0.05 - 1$ ). This rather vaguely indicates the uncertainty is a factor of  $> 20$ . It would be more useful at such an early point of the paper to put a range which includes the lowest reported value to back up the ‘several orders’.”

This should actually read  $0.002 - 1.0$ . We have also added a figure summarising the data points (see response to issue 4, referee #2).

“p 16317, line 1 - ‘calculated using the equation of Schwartz (1986)’ - which equation? Is there not a more recent, accessible (I haven’t been able to obtain a copy of the Schwartz chapter) reference that could be given here? For such an important calculation, surely it would be better to include the equation in the paper.”

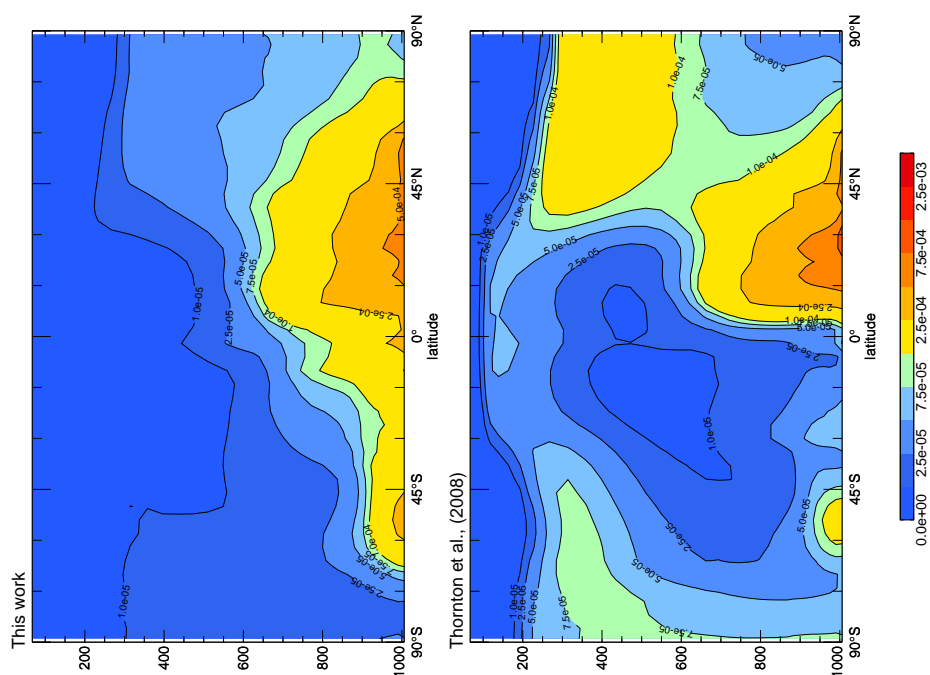
Equation added in.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C9855/2011/acpd-11-C9855-2011-supplement.pdf>

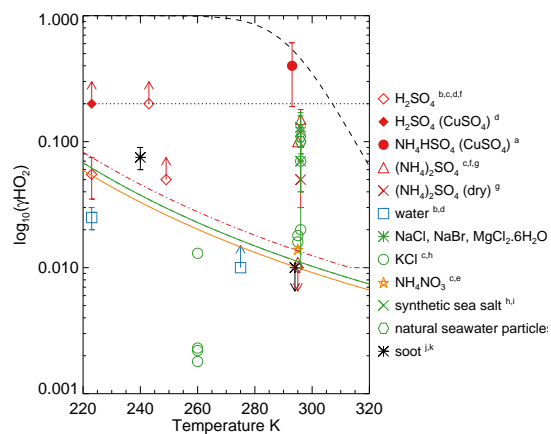
Interactive comment on Atmos. Chem. Phys. Discuss., 11, 16311, 2011.

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**Fig. 1.** Zonal annual mean heterogeneous reaction rates as calculated in the model using the parameterisation presented in this work (top panel) and the scheme of Thornton et al.~(2008) (bottom).

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**Fig. 2.** Summary of laboratory data for  $\gamma_{\text{HO}_2}$  plotted as a function of temperature. Filled symbols denote the aerosol was doped with Cu. The colours represent composition as follows: red indi

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