

Response to the two anonymous reviewers concerning the heterogeneous chemistry modeling assumptions on clouds

Vincent Huijnen

Email: Vincent.Huijnen@knmi.nl

We thank both reviewers for their very critical, but constructive, comments to our manuscript. In brief, they criticize our assumption on model subgrid-scale mixing of ambient HO₂ concentrations and, furthermore, argue that aqueous phase chemistry within aerosols is driven by different processes than within clouds. Different to aerosol, in cloud droplets there is no modeling and observational evidence of H₂O₂ *not* being produced, having significant implications on tropospheric composition. The reviewers suggest to include a sensitivity study on the impact of H₂O₂ production from aqueous phase chemistry. Also the choice of reaction probability γ for clouds was not well chosen, and the first reviewer suggests that the process may be independent the choice of this parameter due to the gas-phase diffusion term acting as the rate-determining steps in the sequence of physical events involved in phase transfer. The reviewer also suggests to do a sensitivity test with different γ to assess the impact of HO₂ loss to clouds.

In response to these concerns, and the comments from J.-F. Müller, we have reviewed and updated our parameterization. We agree with the reviewers that we have been too coarse in our assumptions so far. Below we describe updates to our modeling approach regarding the treatment of HO₂ cloud chemistry, which can be summarized as three main updates, namely: (1) Accounting for subgrid scale (SGS) processes, (2) treatment of the reaction mechanism for aqueous phase chemistry in clouds and corresponding reaction probabilities, (3) the contribution of gas-phase diffusion to the effective pseudo-first order reaction rate.

1. Accounting for subgrid scale processes

As explained before in our first response to Dr. J.-F. Müller, we have reconstructed a HO₂ concentration field that is a best estimate of the assumption of no-mixing within a grid-cell. This assumption is likely more realistic than an instantaneous mixing assumption ($S=CC$), considering the relatively large mixing time scale between cloudy and non-cloudy air as compared to the HO₂ lifetime and can be used to test a subgrid-scale tuning factor. The reconstruction is done by combining two independent 1-day simulations with the C-IFS, where HO₂ concentrations are modeled to be representative either for in-cloud (HO_{2,cloudy}) or outside the cloud (HO_{2,no cloud}). To obtain an estimate for HO_{2,cloudy}, the heterogeneous reaction of HO₂ on cloud droplets (k_{het}) is applied without any scaling to the whole grid-cell. This reaction is switched off to obtain a value for HO_{2,no cloud}. Note that other cloud effects (e.g. perturbations in the photolysis rates) are still accounted for in both runs, which explains the decrease in HO₂ as function of CC, in run HO_{2,no cloud}. Next, the two resulting instantaneous HO₂ concentration fields are scaled with CC to obtain a grid-cell average concentration, according to Eqn. 1, which serves as a best-estimate of grid cell average HO₂ in the situation of no-mixing:

$$HO_{2,no\ mix} = (1 - CC)HO_{2,no\ cloud} + CC\ HO_{2,cloudy} \quad (1)$$

This reconstructed HO₂ field contrasts with the 'instantaneous mixing' (IM) approach as followed in our ACPD manuscript, where the heterogeneous loss rate was scaled using the cloud fraction, rather

than the resulting HO₂ mixing ratios. The mean HO₂ mixing ratios of the various approaches for a single day (1 April 2008), given as a function of CC, are presented in Fig 1.

Nevertheless, for practical reasons a no-mixing approach (NM) i.e. where calculations are performed both for in-cloud and cloud-free chemistry separately within each grid cell, is difficult to achieve in a CTM. Therefore we choose to introduce an empirical SGS scaling factor (S) to be applied to k_{het} , which is defined as a function of cloud fraction (CC):

$$S = CC * \left(1 - \exp\left(\frac{-\beta}{1-CC}\right)\right) \quad (2)$$

Here β is an empirical coefficient that can be used to attenuate S , and hence the reaction rate efficiency, due to SGS variations in the concentration of short-lived species. A large β implies efficient SGS mixing, where Eqn. 2 essentially reduces to $S=CC$. The limited contribution of cloud chemistry to the average heterogeneous reaction rates in each grid-cell (i.e. little SGS mixing, $\beta \rightarrow 0$) for small CC results in $S = \beta * CC$, while for large CC the exponent term becomes zero and thus $S=CC$. The factor β has been tuned in a third run with C-IFS, to match the simulated grid cell average HO₂ concentrations towards HO_{2, no mix}, see Fig 1. It appears that taking $\beta=0.08$ provides the best agreement for our experimental set-up.

The figure illustrates that the introduction of Eqn. 2, as compared to an instantaneous mixing approach, has a significant impact on the chemical reaction budget. This is due to the dominance of grid cells with low CC , where the reaction attenuation modification is maximal. The impact of Eqn. 2 to the chemical budgets is additionally illustrated in Table 1 for different assumptions of β . It shows that for $\beta = 0.08$, the heterogeneous uptake of HO₂ on cloud is decreased by ~67% as compared to an ‘instantaneous mixing’ assumption ($S=CC$). However, this table also indicates that there is a significant sensitivity to this tuning parameter, effectively doubling in size the reaction budget when varying β from 0.05 to 0.16.

This shows that treatment of SGS effects is necessary not to over-estimate the heterogeneous loss rate for free-radicals and chemical species which have a short chemical lifetime compared to the lifetime of clouds. Nevertheless, even though we have confidence in this method for our application, the introduction of Eqn. 2 displays a clear source of uncertainty. We believe that the grid-cell average attenuation of any heterogeneous reaction rate due to SGS effects depends on many physical and numerical factors, such as the assumed time scale of cloud mixing, the time scale of dominating in-cloud versus cloud-free reaction rates, and the numerical discretization (e.g. the

Table 1. Sensitivity of effective heterogeneous reaction budget of HO₂ upon different assumptions of β in units [Tg HO₂ day⁻¹] for 1 April 2008. The last row shows results for the assumption $S=CC$.

β	HO ₂ +CLD
0.05	0.49
0.08	0.62
0.1	0.69
0.16	0.87
inf	1.88

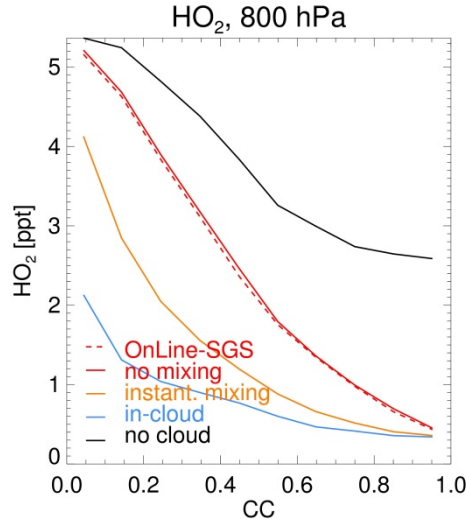


Figure 1. The average HO_2 volume mixing ratios at 800hPa for 1 April 2008 in C-IFS as sampled from global instantaneous 6-hourly fields, and binned for cloud fraction ranges of 0.1. Colour key: Black: No HO_2 uptake in cloud is assumed ($\text{HO}_{2,\text{no cloud}}$), blue: HO_2 uptake reaction is not scaled, i.e. modeled HO_2 is representative for the value within the cloudy fraction ($\text{HO}_{2,\text{cloudy}}$), yellow: HO_2 uptake reaction scales with cloud fraction ('instantaneous mixing'), red solid: Reconstructed HO_2 as best estimate for a 'no-mixing' assumption, red dashed: Modeled HO_2 using SGS mixing assumption given in Eqn 2.

overall chemical time step employed in a model). Therefore, unfortunately it is hard to make general statements on the application and specifically the magnitude of β beyond what is given above, as this would require individual tuning to separate sub-grid scale processes.

2. The aqueous phase reaction mechanism

Thornton et al. (2008) suggest that, in the absence of Transition Metal Ions (TMI), HO_2 is efficiently taken up in aerosol particles, where the dominant aqueous phase chemistry is basically described by partitioning of $\text{HO}_{2(\text{aq})}$ towards H^+ and O_2^- , and the HO_2 self-reaction resulting in the formation of $\text{H}_2\text{O}_{2(\text{aq})}$. Here we assume that the same mechanism holds for the mechanism which occurs in cloud droplets, as is also recommended by IUPAC (Ammann et al., 2013) for heterogeneous reaction of HO_2 in $\text{H}_2\text{O}(\text{l})$. When the cloud droplet re-evaporates this H_2O_2 is thought to be released into the gas phase, resulting into the effective pseudo-first order reaction of:



Thornton et al. (2008) provide a parameterization for this reaction mechanism in terms of the reaction probability (γ). This contains a combination of the mass accommodation coefficient of the gas-phase species into the aerosol bulk phase, α_{HO_2} , and the diffusion and reaction throughout the aerosol bulk:

$$\frac{1}{\gamma} = \frac{1}{\alpha_{\text{HO}_2}} + \frac{3cN_A}{8000(H_{\text{eff}}RT)^2 k_{\text{eff}}[\text{HO}_{2(\text{g})}]r_p} \quad (3)$$

Here the enhanced Henry solubility (H_{eff}) of HO_2 due to its acid-based dissociation is accounted for. The reader is referred to Thornton et al. (2008) for further details of the derivation. The application of Eqn. 3 to cloud droplets ($4\text{ }\mu\text{m} < r_p < 16\text{ }\mu\text{m}$ effective radius, assuming ambient day-time $[\text{HO}_{2(g)}]$ of $10^8\text{ molec cm}^{-3}$, with T ranging between 270-290K, and an average cloud water pH of 5.5), we find a relatively large reaction probability of $\gamma > 0.5$. The essential difference for the reaction probability on cloud droplets as compared to aerosol particles is the assumed pH = 5.5 and the average particle radius ($\sim 10\text{ }\mu\text{m}$, vs $0.2\text{--}2\text{ }\mu\text{m}$ for aerosol particles). This can also be seen from Fig 2 of Thornton et al. (2008). Hence, application of Eqn. 3 to cloud droplets implies a large sensitivity of γ to α_{HO_2} .

Thornton et al. (2008) assume $\alpha_{\text{HO}_2} = 1$, based on a range of measurements on acidic and pH-neutral aqueous surfaces. Also Ammann et al. (2013) recommend $\alpha_{\text{HO}_2} > 0.5$ upon all aerosol types and liquid water, further supported by computations by Morita et al. (2004). Nevertheless, Thornton et al. (2008) warn against the limitations of Eqn. 3 at large γ , writing that ‘the volatilization flux from the condensed phase must remain small compared to other gas-phase sources of HO_2 ’. Furthermore, in their recent work Tilgner et al. (2013) also assume a limitation to α_{HO_2} of 0.01 with reference to Hanson et al. (1992).

In our runs we now also choose to adopt Eqn. 3, where we assume $\alpha_{\text{HO}_2} = 0.5$, in line with IUPAC recommendations (Ammann et al. (2013)). We note that further laboratory investigations are needed to substantiate this value, in order to be sure that we are actually not over-estimating the cloud contribution. On the other hand, the assumption of fully absence of TMI in cloud droplets, which would enhance γ , remains rather conservative (Mao et al., 2013).

3. The contribution of gas-phase diffusion

The pseudo first-order reaction rate constant for heterogeneous reactions is in fact a combination of the gas phase diffusion towards the surface and the reaction probability (γ):

$$k_{het} = \left(\frac{r_p}{D_g} + \frac{4}{c\gamma} \right)^{-1} A \quad (3)$$

With D_g being the gas-phase diffusion constant and c the mean molecular speed. The reviewer suggests that HO_2 loss on clouds may be limited by the gas-phase diffusion rather than by γ . At ambient cloud conditions ($T=273\text{ K}$, $D_g=0.1\text{ cm}^2/\text{s}$ (Hanson et al., 1992), $r_p=10\text{ }\mu\text{m}$) the limitation due to the gas-phase diffusion term indeed becomes dominating for cases when $\gamma > 0.01$. This suggests that little additional sensitivity is expected for γ increasing beyond 0.05 (taking account of the enhanced gas-phase diffusion at smaller effective cloud particle radii). This places a constraint on the maximal impact of heterogeneous chemistry due to cloud droplets which is independent to the discussion of γ (and α_{HO_2}). As suggested by reviewer #1 we have conducted a few short, one day sensitivity runs for 1 April 2008 where we have varied α_{HO_2} between 0.01-0.5, hence directly limiting γ . Here we also limit the reaction rate efficiency because of SGS cloud mixing using Eqn. 2. This results in effective changes towards the dominant HO_2 loss terms as given in Table 2. These test simulations indeed suggest limited additional impact for $\alpha_{\text{HO}_2} > 0.05$, where for these conditions the cloud contribution towards HO_2 heterogeneous chemistry is about half the magnitude as compared

Table 2. Dominant 1 day HO₂ loss terms in [Tg HO₂ day⁻¹] for 1 April 2008 upon different assumptions of α_{HO_2} . The first line refers to the case where HO₂ reaction on cloud is switched off.

α_{HO_2}	HO ₂ +CLD	HO ₂ +Aer	HO ₂ +NO	HO ₂ +O ₃	HO ₂ +OH
N/A	-	1.11	5.62	2.15	1.25
0.01	0.36	1.09	5.52	2.09	1.23
0.05	0.53	1.08	5.48	2.07	1.22
0.1	0.57	1.07	5.46	2.07	1.22
0.5	0.62	1.07	5.45	2.06	1.21

to aerosol. We note that H₂O₂ is produced from cloud heterogeneous chemistry, but this impact to the HO₂ budget terms is not yet fully accounted for in the model due to the short simulation time. Nevertheless, the global O₃ production term (HO₂+NO) is estimated to decrease by 3%, which is a bit smaller than was obtained with the original parameterization.

Summary

In summary, we now adopt Eqn. 2 as a pre-factor to Eqn. 3 in order to account for SGS mixing ($\beta=0.08$). The γ is modeled as specified in Eqn. 3, i.e., the IUPAC recommendation for the heterogeneous reaction of HO₂ on cloud droplets. Here we assume $\alpha_{HO_2}=0.5$ in line with Ammann et al. (2013), but note that gas-phase diffusion term becomes rate-limiting. Note that in the revised model version, the calculation of both cloud and ice effective radius has been updated, as discussed in the second response to J.-F. Müller. Apart from an update in the computation of the mean molecular speed, the computation of the heterogeneous reaction rate on aerosol particles is not changed, where this approach was considered reasonable by the reviewers. With these settings we will fully re-evaluate the system and report on this in an updated version of the manuscript. As a first estimate, the contribution of cloud uptake on HO₂ loss will be about half the contribution of aerosol uptake.

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