

We would like to thank the two anonymous referees and B. Bohn for their helpful comments and suggestions. We have addressed all of these and outlined proposed updates we will make to the manuscript in red below (comments in black):

The authors used measured $j(\text{O}_1\text{D})$ photolysis frequencies as a model input. The $j(\text{O}_1\text{D})$ measurements were made with a filter radiometer on a 22 m tower and were covering downward radiation from the upper hemisphere. In fact, because of low ground albedos upward radiation from vegetated surfaces can usually be neglected in the UV-B range, at least for ground based measurements. The same applies for the tower measurements at Mt. Schmücke in good approximation. However, if the tower is situated into a cloud, upward radiation will increase dependent on cloud optical thickness and tower height. In a very thick cloud the radiation field can become virtually isotropic with up-welling radiation as strong as down-welling. Because of the limited tower height this was probably not the case here, but nevertheless $j(\text{O}_1\text{D})$ could have been significantly enhanced.

To estimate the potential contribution of upward radiation, simulations with the TUV model (also used by the authors) were consulted for the Mt. Schmücke station on 01 Oct 2010 (mid of the campaign period). Spectral actinic flux densities were calculated assuming a range of solar zenith angles (SZA), a typical ozone column of 300 DU, standard aerosol, a ground albedo of 0.02, and an elevation of 937 m. Model output was generated for 959 m representing the tower top at 22 m above ground. Moreover, a homogeneous cloud cover of 1000 m thickness was assumed starting directly at the ground and extending to about 2 km cloud top elevation which is typical for continental stratus clouds. The total cloud optical depth (COD) was varied and from the simulated spectra photolysis frequencies $j(\text{O}_1\text{D})$ were calculated.

In a first step the ratios of downward $j(\text{O}_1\text{D})$ under overcast and clear sky conditions was calculated as a function of COD as shown in Fig. 1. These calculations reveal a non-linear dependence that can be utilized to estimate the COD encountered during the campaign: a reduction by 70% as found experimentally corresponds to a COD of about 30-40. These CODs are in reasonable agreement with those that can be estimated from the liquid water content (LWC) measured at the tower top (Petty, 2006):

$$COD = \frac{3L}{2\rho_l r_{eff}}$$

Here L is the liquid water path, ($L = \text{LWC} \times 1000$ m), ρ_l is the density of liquid water and r_{eff} is the effective cloud droplet radius which was assumed to be 10 μm . LWCs between 0.1 and 0.3 g m^{-3} that were measured at the tower result in CODs between 15 and 45.

In a second step the ratio total/downward $j(\text{O}_1\text{D})$ was calculated as shown in Fig. 2. Here a nonlinear increase is observed. For the COD estimated above the enhancement factor is about 1.2. Consequently, when the tower is in clouds the measured $j(\text{O}_1\text{D})$ should be scaled up accordingly. The same applies for $j(\text{HCHO})$.

We thank B. Bohn for his valuable comment and recommendations for estimating the upwelling radiation present during cloud events which, in the original manuscript, we did not consider. We have scaled the in-cloud measured $j(\text{O}_1\text{D})$ presented in figures 2 and 3 and the in-cloud $j(\text{O}_1\text{D})$ and $j(\text{HCHO})$ used in the analytical expression to determine the first order loss of HO_2 to cloud droplets as suggested. We find, on average, the photolysis rates are enhanced by approximately 17% during cloud events when upwelling is considered. This in turn means that the first order loss process required to reproduce in-cloud HO_2 observations increases modestly from 0.1 s^{-1} to 0.14 s^{-1} on average. Owing to the fact that only minor changes in the first order loss are necessary, we still observe good agreement for the HO_2 uptake coefficient calculated by varying the first order loss in the analytical expression to reproduce HO_2 observations as a function of cloud water pH and the theoretical expression derived by Thornton et al. suggesting that this theoretical expression remains

appropriate to estimate the loss of HO₂ to cloud droplets even when enhancements in radiation are included. All figures and discussions in the revised manuscript will be updated to account for in-cloud enhancements of radiation and we will explicitly reference B. Bohn's comment and include an outline of the methodology for estimating the contribution from upward radiation in the revised manuscript.

1) As pointed out in the comment by B. Bohn, it is not clear whether the authors have taken upward scattering of radiation when the tower was inside a cloud into account in their analytical expression calculating HO₂ concentrations. As stated in the manuscript and illustrated in Figure 1, the FAGE cell was oriented horizontal to the ground to prevent pooling of water on top of the inlet that could enter the detection chamber. On page 23771, the authors state that $j(\text{O}_1\text{D})$ was measured "from the top of the 22m tower, alongside the FAGE detection cell, using a 2_ filter radiometer." It is not clear whether the radiometer was placed on top of the tower near the FAGE inlet but pointed upwards to measure downward radiation, or placed alongside the horizontally oriented FAGE inlet. This should be clarified in the revised manuscript.

The filter radiometer pointed upwards throughout the campaign and so only measured downward radiation. It was located next to the FAGE inlet on the tower. We will clarify this in the revised manuscript along with the corrections we have now made to account for upwelling radiation (please see our response to B. Bohn's comment also).

2) The authors state that the FAGE instrument was calibrated twice weekly during the measurement campaign in addition to calibrations before and afterwards. However, it is not clear that the calibrations were done under conditions that attempt to simulate the water conditions inside the cloud. How did the authors correct their data for quenching by water vapor during the in cloud measurements? During HOxComp, it was found that there may have been an unknown factor related to water vapor that may have influenced the HO₂ instrument sensitivities or may have caused an unknown interference inside the FAGE cells (Fuchs et al., Atmos. Chem. Phys., 10, 12233–12250, 2010). The authors should comment on the potential impact of water on their in-cloud measurements of HO₂.

Calibrations were performed at relevant water vapour concentrations so as to encompass the ambient water vapour concentrations observed. As such, no correction for quenching of the fluorescence signal by water vapour is necessary and has not been made. In the lab we have studied the impact of H₂O (v) on the sensitivity of this FAGE cell type (as outlined by Commane et al. ACP, 10, 8783-8801, 2010) by systematically varying the H₂O from 500 ppmV to 10 000 ppmV and observe only ~ 10 % reduction in sensitivity over this H₂O range for both OH and HO₂ which can be entirely explained by the known quenching of fluorescence by H₂O molecules. We will make a remark reflecting this in the revised manuscript.

3) Incorporating HO₂ uptake onto cloud droplets into the GEOS Chem model leads to significant changes in radical and H₂O₂ concentrations depending on the fate of aqueous HO₂. Figure 10 shows that HO₂ uptake leading to the formation of water reduces surface radical and H₂O₂ concentration (Figure 10a), while HO₂ uptake leading to the formation of H₂O₂ leads to an increase in surface H₂O₂ and less of a reduction in radical concentrations (Figure 10b). However, the column radical and H₂O₂ concentration changes appear to show the opposite when HO₂ uptake is incorporated into the model (Figure 11). In this Figure HO₂ uptake leading to the formation of water leads to an increase in the column H₂O₂ concentrations and less of a reduction in radical concentration (Figure 11a), while HO₂ uptake leading to H₂O₂ formation leads to a decrease in the column H₂O₂ and a greater reduction in the column radical concentrations (Figure 11b). On page 23778 the authors state

referring to the concentration of OH that “changes to the column values are only significant in the case where H₂O₂ is not produced.” However, in Figure 11a (HO₂ uptake leading to water) the column values of OH do not show a significant reduction, while a significant reduction in column OH is shown in Figure 11b (H₂O₂ produced). Are the results in Figure 11a and b reversed? The authors should clarify their discussion of these model results.

Regrettably, we have labelled Figure 11 incorrectly and as spotted by the referee Figure 11 a) actually represents the annually averaged fractional change in column HO₂, OH and H₂O₂ with the inclusion of HO₂ uptake to clouds leading to the production of H₂O₂, whilst b) represents the column change with the production of H₂O. We will correct the figure caption in the revised manuscript.

Title: Seems a bit too broad for the actual content of the paper and could be more specific to include a direct mention of observations in cloud.

We propose ‘The influence of clouds on radical concentrations: Observations of OH and HO₂ during the Hill Cap Cloud Thüringer (HCCT) campaign in 2010’ as an alternative title.

Introduction: I do not see the classic paper by Jacob on cloud chemistry. Jacob, D. J. (1986), Chemistry of OH in remote clouds and its role in the production of formic-acid and peroxymonosulfate, J. Geophys. Res.,91(D9), 9807– 9826.

This is an oversight, we will refer to the results from this classic paper on cloud chemistry in the introduction of the revised manuscript.

p 23776 end and 23777 beginning: The comparison of derived gamma values for uptake to cloud droplets with laboratory measurements on aerosol particles is somewhat of an apples/oranges problem. The aerosol particles probed in the lab will have very different ionic contents at the very least, and possibly phase (depending on the experimental conditions). That they agree well or not with values derived in cloud is therefore somewhat inconsequential.

We agree that we are not comparing like with like. However, as no laboratory studies have been performed which look at the uptake of HO₂ to cloud droplets, we feel this is the closest comparison we can make. Many of the lab studies have been performed on aqueous aerosol. We will narrow the comparison down to laboratory measured uptakes observed on aqueous aerosol in the revised manuscript.

p 23778, line 16. I think the value of gamma = 0.2 in GEOS-Chem goes back at least to Martin, R. V., D. J. Jacob, R. M. Yantosca, M. Chin, and P. Ginoux (2003), Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, J. Geophys. Res., 108(D3), 4097, doi:10.1029/2002JD002622.

The value of the gamma for HO₂ onto aerosol in the standard version of GEOS-Chem has some history. The model has used the Thornton et al., parameterization in the past, and very high values derived by Mao et al. 2013 (Mao, J., S. Fan, D.J. Jacob, K.R. Travis, *Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols*, *Atmos. Chem. Phys.*, **13**,509-519, 2013b.) Given the uncertainties in the value of the gamma the Model Steering Committee now considers a uniform value of 0.2 to offer the advantage of simplicity. Thus we have returned to the Martin et al value but via a path which has taken us through Thornton and Mao. We will include this reference for the gamma value used in GEOS-Chem in the revised manuscript.

Figure 4 - is the data in this figure a compilation of many different cloud events, or is it one cloud event where the surface area might be correlated with time and

This data is a compilation of all daytime cloud events. We will update the text to clarify this.

pg 23778, line 11, missing a reference after "Thornton".

This will be included.

1. I'm quite surprised there is such a large effect upon "surface" HO₂ due to clouds, especially large in the mid and higher latitudes. Are these results the effects of HO₂ uptake to both aerosol and cloud relative to no uptake, or really just the effect of uptake to cloud only, on top of an uptake to aerosol at $\gamma = 0.2$? These results should be compared to those from Thornton et al 2008, McIntyre and Evans, Martin et al 003, etc focused upon the effect of HO₂ uptake to aerosol particles. Aerosol particles are more likely distributed throughout the vertical near the surface than cloud (outside of fog situations anyway), and the impacts of having fast uptake of HO₂ to aerosol particles were comparable to those reported here.

The plots do show the difference between simulations with HO₂ uptake onto clouds and those without. We note that the magnitude of the changes calculated here are generally consistent with the simulations presented in (Huijnen et al., 2014, Atmos. Chem. Phys. Discuss., 14, 8575–8632, 2014 www.atmos-chem-phys-discuss.net/14/8575/2014/ doi:10.5194/acpd-14-8575-2014) although the figures in Huijnen et al are not directly comparable with our plots. We now include a plot of the liquid water mass concentrations in the model both as a zonal mean and column integrated in the publication to show that in the GEOS-5 met fields there is significant liquid water in the lowest most levels of the model leading to the uptake.

2. The question is for such a short lived species like HO_x, how do cloud, presumably located at the top of the boundary layer or higher, affect surface HO₂ concentrations? Does HO₂ loss in cloud become a major sink of boundary layer O₃ in the model, and therefore impacts the HO_x production outside of cloud? Liang and Jacob JGR 1997 found little impact of cloud chemistry on ozone over N. America, which seems somewhat consistent with the results presented here. In fact, Liang and Jacob mention the impact of cloud chemistry on ozone might be significant in stratus capped marine boundary layer regions. It would be helpful to therefore show the perturbation to modeled surface O₃ due to incorporating HO₂ uptake in cloud in the model. I assume this output from the model already exists and new simulations would not be needed.

We now include plots of the impact on O₃ concentrations in our figures. The impact on O₃ is minor globally as the regions where HO₂ is perturbed the most are the regions where the HO₂ lifetime is long as the NO concentration is low. Thus the impact over ozone production areas is minimal and the impact on O₃ destruction is small. Impacts are highest where there are clouds over low NO_x area.

3. How were the cloud fields in GEOS-Chem prescribed? Were they fixed between simulations of uptake/no uptake so as to represent the exact same radiation fields and vertical distributions, etc? Does GEOS-Chem realistically represent air mass transport through cloud and thus the average time air spends within cloud?

The model prescribes the cloud liquid water in each grid box from the GEOS-5 Meteorological analysis. Thus the impact of clouds on the radiation field and the vertical distribution of the clouds will be identical in all simulations. The model representation of cloud processes is by necessity of the grid resolution (~250km) fairly crude. However other studies which need to invoke cloud chemistry within the model (notably for SO₂ oxidation) suggest that the model is capable of reproducing these features with some fidelity (see for example Alexander, B., D.J. Allman, H.M. Amos, T.D. Fairlie, J. Dachs, D.A. Hegg and R.S. Sletten, Isotopic constraints on sulfate aerosol formation pathways in the marine boundary layer of the subtropical northeast Atlantic Ocean, *J. Geophys. Res.*, 117, D06304, doi:10.1029/2011JD016773, 2012).

4) This section should be expanded to address the above, and also include a discussion on the impact of HO₂ uptake in cloud upon the tropospheric ozone burden.

We now include such a discussion.