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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of clouds on the oxidising capacity of the troposphere" *by* L. K. Whalley et al.

Anonymous Referee #2

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This paper describes a very nice set of experimental observations of gas-phase HO2 within cloud, obtained at one mountain site in Germany. The observations show a clear dependence of the HO2 concentration upon condensed phase surface area in the cloud. The authors use this dependence to test the current understanding of HO2 multiphase chemistry and provide compelling evidence that known aqueous phase chemistry of HO2 is rather accurate and complete - at least for the type of conditions sampled. The conditions seem rather typical for continental boundary layer cloud - mildly acidic and liquid water phase. Interestingly, the authors did not need to invoke trace metal catalyzed chemistry to explain the observed decay of HO2 with cloud surface area. The paper is reasonably well written (some references missing, some content and discussion needs to be added), the experimental results are compelling, and the

topic is of interest to the atmospheric chemistry community. I recommend publication after revisions are conducted to address the following comments.

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.

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.

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.

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.

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

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

Global impact calculations with GEOS-Chem -

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

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2003, 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.

2. The question is for such a short lived species like HOx, 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 HOx 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.

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?

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23763, 2014.