Atmos. Chem. Phys. Discuss., 14, C8763–C8765, 2014
www.atmos-chem-phys-discuss.net/14/C8763/2014/

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 #1

Received and published: 3 November 2014

This paper presents measurements of HO_2 concentrations made from a mountain top during the HCCT-2010 campaign. Measurements were done using an LIF-FAGE technique both in and out of clouds to derive an uptake coefficient of HO_2 to cloud droplets. The measured HO_2 concentrations made out of clouds agree well with a simple empirical model during the day, but the measurements made inside of clouds were significantly lower than the model. Taking the decrease in $j(O^1D)$ into account, the authors demonstrate that the measured concentration of HO_2 decreases with increasing cloud droplet surface area, suggesting that heterogeneous loss of HO_2 must be occurring on cloud droplets.

The authors find that adding an additional pseudo-first order loss rate of 0.1 s^{-1} to their model brings the predicted HO_2 concentrations into reasonable agreement with

the measurements. They find that this loss rate corresponds to an uptake coefficient that is consistent with laboratory measurements of heterogeneous HO_2 loss as well as theoretical calculations based on aqueous phase chemistry of HO_2. The authors also compare their measurements to predictions from a detailed trajectory model that includes updated multiphase chemistry (SPACCIM). They find that the trajectory model is also able to reproduce the observed HO_2 concentrations during a single cloud event using a mass accommodation coefficient of 0.01.

These results confirm that clouds may significantly reduce radical concentrations as previously suggested. To determine the potential impact of clouds on the oxidizing capacity of the atmosphere, the authors show GEOS Chem results where the model was updated to include HO_2 uptake by clouds. The model results suggest that uptake of HO_2 on clouds could significantly reduce surface radical concentrations, especially in the extra-tropics.

The paper is well written and suitable for publication in ACP after the authors have addressed the following comments:

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 HO_2 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 $j(O^1D)$ was measured "from the top of the 22m tower, alongside the FAGE detection cell, using a 2π 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.

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

ACPD
14, C8763–C8765, 2014

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 HO_2 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 HO_2.

3) Incorporating HO_2 uptake onto cloud droplets into the GEOS Chem model leads to significant changes in radical and H_2O_2 concentrations depending on the fate of aqueous HO_2. Figure 10 shows that HO_2 uptake leading to the formation of water reduces surface radical and H_2O_2 concentration (Figure 10a), while HO_2 uptake leading to the formation of H_2O_2 leads to an increase in surface H_2O_2 and less of a reduction in radical concentrations (Figure 10b). However, the column radical and H_2O_2 concentration changes appear to show the opposite when HO_2 uptake is incorporated into the model (Figure 11). In this Figure HO_2 uptake leading to the formation of water leads to an increase in the column H_2O_2 concentrations and less of a reduction in radical concentration (Figure 11a), while HO_2 uptake leading to H_2O_2 formation leads to a decrease in the column H_2O_2 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 H_2O_2 is not produced." However, in Figure 11a (HO_2 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 (H_2O_2 produced). Are the results in Figure 11a and b reversed? The authors should clarify their discussion of these model results.

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