Response to reviewer's comments – second iteration

Some comments/Requests from the Editor:

Referee 1.

In response to the referee you say:

"The observed-to-modeled HO2 ratio shows little evidence of a NO-dependence. The reanalysis of Olson et al. (2006) explains the NO-dependence of the ratio discussed in Faloona et al., (1999), and the NO-dependence observed often in ground-based studies is not evident until NO exceeds 3-5 ppbv. Because the highest NO mixing ratio encountered in DC3 was about 3 ppbv, we would not expect to see this effect in the DC3 results."

Editor: Could you please give some very brief details in the revised MS about how the "re-analysis" by Olson et al. 2006 "explains" the NOx dependence of the measured/modelled HO2 ratio. Could you also please cite the other studies where substantial deviations observed during ground-based studies typically are not evident until NO exceeds 3 ppbv.

We expanded this discussion to include results from INTEX-A and moved the discussion from section 3.1, last paragraph to section 4.1 Comparing DC3 to Previous Studies, second-to-last paragraph.

"For DC3, observed and modelled HO_2 appear to agree as a function of NO up to about 2 ppbv, which are the highest NO values encountered. For several previous ground-based studies, the observed HO_2 was not obviously greater than the modelled HO_2 until NO reached ~2 ppbv or greater (Martinez et al., 2003; Ren et al., 2003; Shirley et al., 2006; Kanaya et al., 2007; Brune et al., 2016). For aircraft studies, in some cases the observed HO_2 did not obviously exceed the modelled HO_2 until NO approached 2 ppbv (Bair et al, 2017), while in other studies, the obvious exceedance occurred when NO was only a few hundred pptv (Faloona et al., 1999; Ren et al., 2008). Olson et al. (2006) showed that the Faloona et al. (1999) results for the SUCCESS campaign could be explained by the averaging of sharp plumes containing high NO and depleted HO_2 with the surrounding air. They showed that the SONEX results could be mostly explained by including all HO_x precursor observations and updated kinetic rate coefficients and photolysis frequencies in the model. For INTEX-A (Ren et al., 2008), the enhanced NO is in the upper troposphere, where the observed-to-modeled HO_2 reached a factor of 3. It is possible that the HO_2 calibration was in error at low pressure (i.e., higher altitudes), although observed and modelled HO_2 agree in the stratosphere. It is also possible that there were missing HO_2 sources or outdated reaction rates in the model chemistry. We intend to re-examine INTEX-A and other previous NASA DC-8 missions that included ATHOS to see if an updated model can better simulate these HO_2 observations. "

For your response to another of the comments:

"We agree that this is an interesting study to do, but it not within the scope of this paper. However,

we did a quick check on this idea by calculating the observed-to-modeled HO2 ratio, filtering it for altitude bins (i.e., 5-8 km, 8-10 km, >10 km), and solar zenith angle bins (i.e., 50o-60o, 60o-70o, 70o80o), and then plotting it as a function of J(O(1D)). In all cases, the ratio was constant as a function of J(O(1D)). This observation indicates that using the measured photolysis frequencies accurately captures the HOx production by photolysis as seen in Figure 4e."

Editor: Could you incorporate aspects of this response into the revised MS as it is an interesting finding you have stated.

In the last paragraph in section 3.1, we have rewritten it to include this observation and an observations of differences in observed and modeled HO_2 that was found for O_3.

"Another good test of the model photochemistry is the comparison of measured and modeled OH and HO_2 as a function of controlling variables (Fig. 4). The photolysis frequency for O_3 producing an excited state O atom, $JO(^1D)$, and O_3 are both involved in the production of OH. O_3 and NO cycle HO_2 to OH, while modeled OH reactivity cycles OH back to HO_2. In general, measured and model OH and HO_2 agree from $2x10^{-6}$ s^{-1} to $7x10^{-5}$ s^{-1} for $JO(^1D)$, from $2x10^{-3}$ ppbv to $7x10^{-1}$ ppbv for NO, from 40 ppbv to 100 ppbv for O_3. For $JO(^1D)$ greater than $2x10^{-5}$ s^{-1}, the median observed-to-modeled HO_2 ratio is 0.98; the in-cloud ratio is an insignificant 10% less than in clear air, indicating that the observed photolysis frequency measurement is accurate even in clouds. The observed-to-modeled HO_2 ratio shows little evidence of a NO-dependence, although observed-to-modeled HO_2 exceeded 2 for ~2% of the values when NO was more than 0.5 ppbv. For the O_3 observations greater than 200 ppbv, which are 0.5% of all observations, the observed-to-modeled HO_2 and OH are both ~0.5. It is possible that the behavior as a function of controlling variables is also a function of altitude. However, with the exception of low values of $JO(^1D)$, the median observed-to-modeled OH and observed-to-modeled HO_2 are generally independent of both the controlling variables and altitude (Fig. S4). The observed-to-modeled OH and HO_2 are also independent of whether the measurements were made in Colorado, Texas/Oklahoma, or Alabama (Fig. S5), although the ratios for some altitudes vary widely due to fewer data points in the altitude medians."

Referee 1 also says:

page 8, line 6: The table showing the measurements is missing. It should be presented in the main paper. Accuracies and time resolution of the measurements should be given.

Editor: I agree with the referee that the Table belongs in the main paper. The table includes for example accuracy and time resolution of the main measurements which are modelled (OH, HO2) and the species included in the model (e.g. VOCs) – these are central pieces of information. Also in Table 1 it is not clear what the references mean, as some of these are quite old, e.g. 1991. Could you please indicate in the caption what the reference actually refers to? For example, is it a description of the instrument used on the aircraft for the measurements? (this is not clear owing to the date of *the reference being quite old in in some cases)*

We feel that this table belongs in the Supplementary Material, but will move it.

We thought that it was clear that the Reference was the reference describing the instrument, but have added the words "that describes the instrument" to the heading. Some references are quite old because the technique and the core instruments are quite old but have been constantly improved.

Referee 1 makes a point about there being additional VOCs in the convective outflows following rapid uplift…

…. is especially relevant in the outflow of convective clouds which can transport relatively short-lived species to higher altitudes in short time.

Referee 2 makes a similar comment about convective outflows where this may impact on the interference seen in the ATHOS instrument:

"On page 6, the OH and HO2 interferences suffered by ATHOS are discussed and the authors state that interferences are only significant above forests and cities and are negligible outside of the planetary boundary layer. The authors should comment on whether this statement remains valid when sampling in and around convective clouds which can rapidly transport air from the surface. The correction applied to the HO2 observations to account for RO2 interferences is rudimentary and more details should be provided on the type of RO2 species present. The correction will change with changing RO2 species present and this relies on model predictions for RO2 which is far from ideal"

Editor: Although in your response you discuss the method you use for correcting for RO2 interferences, the MS still states that interferences are only significant just above forests and cities and is negligible above the PBL. Can you please modify this statement to say that interferences may also be important in the convective outflow at higher altitudes where VOC concentrations are higher owing to rapid uplift.

In section 2.2, 4th paragraph, we add a sentence capturing these concerns.

"On the other hand, the deep convective clouds encountered in DC3 can lift short-lived VOCs that cause the HO_2 interference to the upper troposphere. Because the ATHOS was still sensitive to this RO_2 interference in DC3, we are not able to determine if this interference is affecting the HO_2 observations around and in these clouds."

Referee 2 says:

Pg 14, line 1: What was recalibrated in the instrument? The phototube? The authors *should comment on why they think it is appropriate to apply a calibration performed so long after the campaign.*

Your response:
Looking back through the notes for DC3, we noticed that the procedure had not been followed completely and that the transmission of the window between the calibration lamp and the calibration flow tube, which is 0.86, had not been included in the calibration. We re-measured the window transmission and confirmed that it was still 0.86 and then applied this number to the OH and HO2 calibration.

Editor: Please give some brief detail on the reason for recalibration in the revised MS as readers will be wondering the same as the reviewer.

In section 3.5, 3rd paragraph, we add a sentence giving this reason.
"This recalibration was needed to account for the window absorption of calibrated 185 nm radiation that was neglected in the initial DC3 calibration."

Editor:
Other comments:
In the revised MS, you have the text:
We have rewritten Section 4.2, 2nd paragraph as
"In DC3, the DC-8 spent hours flying in anvils of the cumulus clouds, which consisted of ice particles. DC3 provides evidence that the HO2 uptake on ice is small. These results are consistent with HO2 results over the western Pacific Ocean (Olson et al., 2004) but not with those over the northern Atlantic (Jeaglé et al., 2000). In Mauldin et al. (1998), a large difference between the observed and modeled OH was found in clouds, but this difference may have been due to the lack of photolysis frequency measurements, which are crucial to test photochemistry in a cloudy environment. In DC3, the DC-8 spent essentially no time in liquid clouds, for which there is evidence of measurable HO2 uptake (Olson et al., 2006; Whalley et al., 2015). Thus these DC3 results provide constraints of HO2 uptake on aerosol and ice particles, but not on liquid water particles."

Editor: The following paper ought to be cited and briefly discussed here, as it shows that the HO2 concentration is reduced when the aircraft sampled clouds, and the concentration was reduced *more than expected owing to the reduction in J(O1D), providing some evidence for heterogeneous uptake which was not included in the calculation of [HO2]. The liquid water measurements shows these are primarily liquid clouds.*

Commane, R., Floquet, C. F. A., Ingham, T., Stone, D., Evans, M. J., and Heard, D. E.: Observations of OH and HO2 radicals over West Africa, Atmos. Chem. Phys., 10, 8783-8801, https://doi.org/10.5194/acp-10-8783-2010, 2010.

We added the reference. In the Introduction we add the following sentence to paragraph 5.
“During the African Monsoon Multidisciplinary Analyses (AMMA) campaign, daytime HO_2 observations were generally simulated with a photochemical steady-state model, but not in clouds, where modeled HO_2 greatly exceeded observed HO_2 (Commane et al.,2010), suggesting HO_2 uptake on liquid cloud drops.”

Also:
““Modeled RO2 is primarily CH3O2 and CH3CHO2 above 5 km.”
Change to CH3CH2O2
Typo fixed.