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Discussions

Interactive comment on "Atmospheric Oxidation in the Presence of Clouds during the Deep Convective Clouds and Chemistry (DC3) Study" *by* William H. Brune et al.

Anonymous Referee #2

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General comment

The manuscript describes airborne observations of OH, HO2 and OH reactivity during the DC3 project. The authors conclude that the generally good agreement between model predictions and the observations provides evidence that current photochemical models can simulate atmospheric oxidation even around clouds. Due to the large number of minor corrections that I came across during the review, however, along with a few more serious concerns, I remain to be convinced by the conclusions drawn. I hope the authors are able to adequately address the comments and corrections below before the final publication.

Major comments

The authors report short scattering signals by cloud particles which occur randomly both during online and offline measurements and discuss the treatment of the raw data to reduce the noise from these large scatter signals in section 2.2. Could the authors comment on whether this approach introduces any bias into the analysis, given that the online measurement period is 3 times longer than offline? The authors should provide a comment on the choice of exceeding the average background signal by four standard deviations. Would a different limit change the results?

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.

Pg 12, section 3.3: Why was HONO photolysis not considered for OH production?

On page 14 the authors calculate P(O3) from the 'observed HO2 + modelled RO2' and from 'modelled HO2 + modelled RO2' and compare to the 'observed O3 change'. Lines 16 and 17 state that HO2 accounts for a little more than half the total O3 production, but then lines 21 – 23 state that the observed O3 change was equal to 14 ppbv and the P(O3) calculated from the observed HO2 was 14 ppbv (figure 9 seems only to show P(O3) calculated using HO2)? What was the contribution of modelled RO2 to P(O3)? Are the authors suggesting that roughly half of the ozone produced partitions to NO2? Could the change in NO2 over the flight leg be shown to corroborate this?

Minor corrections

Pg 2, lines 17 – 20: Reads as though nitric oxide is needed to produce RO2 and HO2 from OH oxidation of VOCs, this isn't the case.

Pg 3, lines 9 – 11: HO2 interferences in LIF systems can now be minimised, however, this sentence suggests that HO2 measurements are still affected by interferences. This needs to be corrected.

Pg 4, lines 1 – 2: I find this sentence confusing as metal ions enhance the HO2 uptake probability rather than reduce it.

Pg 5, line 15: 'lower' than what?

Pg 5, line 21: Provide the concentration of NO that is added.

Pg 9, line 14 & 15: Surface area is not a concentration. Please include the mean surface area.

Pg 9, line 24: Which organic peroxy radicals + OH reactions does the model include?

Pg 11, E3: k'OH should be defined absolutely. Does it just include OH + CO and OH + HCHO that lead to HO2 directly or are VOC reactions that cycle to HO2 via RO2 considered too? If it is the latter, the authors should comment on the validity of this approximation under low NO conditions.

Pg 11, line 20: Is this ratio from measurements or the model?

Pg 11, line 22: what is the uncertainty limit?

Pg 11, line 27: 'factor of 600 for JO(1D), a factor of 100 for NO..' it is not clear from these statements the range of photolysis rates or concentrations over which the model agrees with the observations. I suggest providing the range in the text.

Pg 11, line 28: 'One exception is OH for NO greater than 1 ppbv..' Are the observations greater or less than the model in this case?

Pg 12, line 3: Please provide the limit of detection here.

Pg 12, line 7: 'modeled OH reactivity looks quite similar..' Could % differences or differences in s-1 be given here?

Pg 12, line 8: what loss rate is assumed for the model generated intermediates?

Pg 13, line 22: 'substantial agreement' – could this be given as a % agreement?

Pg 13, line 29: provide figure number.

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.

Pg 14, E3: should be E4. Also, please define L(O3) in the text.

Pg 16, line 1: '..HO2 calibration at low pressure was in error' wasn't a calibration over a range of pressures performed?

Pg 16, line 9: during which campaign was the fire plume observed?

Pg 16, line 21: add '3' after 'DC'

Pg 16, line 26 – 27: My understanding of the Whalley et al, 2015, mountaintop cloud study was that the uptake coefficient reported was determined from the observed decrease in the measured HO2 and was not calculated from the size, composition, etc of the aerosol/cloud droplet as is suggested in lines 26 and 27. The authors should compare the uptake coefficients determined rather than the level of decrease in HO2 given the very different surface areas encountered in the different campaigns.

Pg 16, line 28: 'small cloud impacts on HO2 are consistent..' this statement is at odds with the comment in the Introduction (pg 3, lines 19 – 22) which states that an observed to modelled ratio of 0.65 was reported during the in-cloud measurements in Olson et al (2006). Please clarify.

Pg 17, lines 9 – 11: was data missing when the model and measurements diverge?

Pg 17, line 23: remove 'strong'.

Figure 6: the dots representing 'obs loss' and 'obs prod' are very difficult to distinguish from each other. I suggest more contrasting colours are used. The modelled loss should be added to this figure too.

Figure S1 highlights the disagreement between OHRobs and OHRmod. If the modelled OHR was forced into agreement with the OHR observed, how would this impact the modelled OH (and the level of agreement with OH observed)?

Figure S1 – S6: The fitted line should be added to the OHR scatter plots.

Figure S8: is OH+NO2 considered as a loss?

Figure S9: could the temperature profile be added?