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## ***Interactive comment on “Evidence for***

# **heterogeneous chlorine activation in the tropical UTLS” by M. von Hobe et al.**

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Review of von Hobe et al., Evidence for heterogeneous chlorine activation in the tropical UTLS

I found this paper to be extremely well written, informative, important, and also somewhat provocative. I suggest publication after minor revisions.

The authors present an analysis of measurements of ClO, O<sub>3</sub>, NO<sub>x</sub>, NO<sub>y</sub>, H<sub>2</sub>O (gas and condensed), particles, etc in the tropical tropopause. The observations show strong evidence for heterogeneous activation of chlorine, which could be quite impor-

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tant for understanding ozone trends in this region of the atmosphere.

I shall first state what I like most about the paper, then state what I like least about the paper :).

I most like:

- a) the observations themselves
- b) the very thoughtful descriptions of the theory that might describe the observations, including a very nice examination of uncertainties, that represents a large step forward

I least like:

- a) that it is hard to relate figures 7 and 8 to the observations (why are there no data on the panels and why is measured O<sub>3</sub> not noted in the caption?);
- b) the explanation of ClO and NO<sub>x</sub>. I find it hard to believe that ClO in the tropical UTLS is insensitive to NO<sub>x</sub> . . . if calculations supporting this view exist (pg 18081, line 22), they should be shown
- c) that potential troublesome issues like high ClO at night are mentioned but kind of “swept under the rug”
- d) that the paper does not address, in any way, whether VSL (very short lived) species might be supplying the Cl that leads to the observed ClO

I suspect points a), b), and c) will be easier to address than point d). No need for specific responses to these points as they are re-iterated below.

I thought this distillation, at the start, would serve as an appropriate introduction to the review. Overall, I really really like the paper, even though the “least like” section above contains more points than the “most like” section.

Major comments:

- 1) If possible (and it may not be), can the authors say something about the possible

supply of Cly from decomposition of VSL species to this region of the atmosphere? This may be a challenge. In a CCM that considers supply of Cly from the 12 long lived sources considered by WMO, would we expect to have as much Cly in the sampled tropical lowermost stratosphere as is assumed in the model?

2) Page 18081 puts forth an explanation as to why ClO would not depend on NOx. I am not convinced. Seems to me that if an airmass has elevated ClO and elevated NO<sub>2</sub> is introduced by lightning, these species should react quickly to form ClONO<sub>2</sub>, and the “game is over” regarding elevated ClO. Hence, the observation of high ClO in the presence of high NO<sub>2</sub> is puzzling. Is it that low O<sub>3</sub> titrates chlorine to Cl ?!? The authors refer to calculations supporting their explanation, and showing that NOx returns to HNO<sub>3</sub>, bypassing ClONO<sub>2</sub>. Would appreciate if these calculations could be critically assessed and shown as a new figure. This result seems counter-intuitive . . . I am not saying it is wrong . . . but, it is worthy of a figure and a more detailed explanation.

3) Page 18076 states:

Interestingly, the observations on 30 November were made in darkness (SZA>100), where significant amounts of ClO are unexpected.

The next page states:

For the runs with 200 ppb O<sub>3</sub>, CLaMS BT predicts ClO to be present in significant amounts during night-time, together with the main night-time reservoir species OCIO.

I suggest adding SZA to Figure 6, which will aid the interpretation of the data. Also, the statement about CLaMS BT ClO should be more quantitative: does not model find amounts of ClO at night comparable to what was observed. If so, please state this. If not, this too should be stated.

It is very important to establish whether the amount of ClO reported at night can be supported by theory. If so, am very interested in why conversion of ClO to nighttime reservoirs is suppressed. If not, thus raises a question about whether the “report” of

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significant levels of ClO at night could be due to heterogeneous conversion, on the inlet of the instrument, of another inorganic chlorine species to either ClO or a gas the instrument records as being a signal from ClO. If this is the case, then such a conversion process could be happening for other flight segments. This could effect some details of the theoretical explanation, although I suspect the need to invoke heterogeneous processing would persist.

## Minor points

1. Page 18065, line 26: should probably either write “e.g., Solomon et al.” or else add a citation to the Keim et al. 1996 paper, and perhaps a few others.
2. Page 18066, line 3: this is a long sentence that should perhaps be broken into two. Also, would say “significant amounts of ClO due to heterogeneous activation are expected to be present . . .”
3. Page 18066, lines 9 and 10: “exists” should be “exist” and “has” should be “have”
4. Page 18067, line 4: Suggest inserting a sentence giving altitude range of the Geophysica. “Super-high-altitude” means different things to different people :)
5. Page 18067, lines 18 and 20: text states “chlorine atoms” one place and “Cl atom” later. Better to be consistent.
6. Page 18067, line 23: Suggest new paragraph at “More critical . . .”
7. Page 18068, lines 3 and 4: one phrase uses “2-10” and another uses “1 to 30” . . . again, consistent usage would be better.
8. Page 18068, line 12: suggest “periodic”
9. Page 18069, line 8: “permits to avoid” is not be clear.
10. Page 18072, line 20: the disabling of the ice in the simulation discussed here seems inconsistent with later discussion, page 18074 (lines 5 and 6), where “reactions

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were allowed to occur on ice". I think rxns on ice are disabled only for the steady state calculations of noon time ClO. A definitive statement to this effect would be helpful.

11. Page 18073, line 19: strongly suggest the difference between observed T and ECMWF be quantified. The phrase "significantly colder" is not adequate. Also ... is there a reference for the measurement of temperature? (none is given on page 18069)? How accurate is the measurement? The analysis in this paper hinges on proper knowledge of temperature, so more detail is needed.

12. Page 18073, line 22. The initialization of total H<sub>2</sub>O to 10 ppm seems high. Why was this value picked? Are model results sensitive to this value? Suggest that the sensitivity to initial total H<sub>2</sub>O be stated and, if there is a sensitivity, consider expressing this in Figure 10.

13. Page 18075, lines 16 and 17: text states "the highest degree of chlorine activation ... was found in air masses with low ozone but also very low temperatures (Fig. 4)".

I see much more support for the low O<sub>3</sub> relation in Figure 4 than I do for the low temperature relation. The non yellow points are only present for low O<sub>3</sub>; they span the entire range of temperature.

Nowhere is  $x(\text{ClO})/x(\text{Cl})$  versus T plotted.

Strongly suggest adding such a plot. Also, suggest exploring  $x(\text{ClO})/x(\text{Cl})$  versus min T along trajectory. Statements in the paper would be much easier to evaluate with these two plots.

14. Page 18076, line 15 and line 24. In the discussion of Figure 6 and Figure 7, the text starts describing the scientific interpretation of the data, before the figures are actually described. To understand, I had to stop reading the text, study the captions, then return to the text. If space permits, paper would be easier to read if the figures are described before they are interpreted.

Also, Figures 7 and 8 are very hard to understand without any representation of data

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on the figure or caption. Strongly suggest adding data, as appropriate, to the panels (on day 0) and/or in the caption. I am tempted to elevate this to a “major point”, but shall leave here.

15. Pages 18077 to 18079: Sorry Marc et al., I have not had time to go through the details of the chemical equations. The argument seems plausible. I just want to be honest that I have not “checked” the symbolic representation of the chemistry.

16. Page 18080, line 16: Please clarify exactly what is uncertain by about a factor of 3. If it is ClO/Cly, then it is hard to see how the upper limit can be 3x higher than the baseline, as ClO/Cly can not exceed unity. Easy for me to see how ClO can be uncertain by a factor of 3, if uncertainties in Cly are considered.

17. Page 18080, line 19: Consider new paragraph at “To illustrate”

18. Page 18081, lines 13 and 14: One notable omission is the lack of discussion about whether 5 ppt of Bry is plausible. Citation to Dorf et al. bottom of page 18064 does not say much. A sentence or two could be added discussion this :)

19. Figure 2: I assume red represents Scout-O3 and green TROCCINOX, based on Figure 3. This should be clarified within Figure 2.

20. Figure 5: Can representative error bars for  $x(\text{ClO})/\text{X}(\text{Cly})$  be added? I realize you can not show for all points ... but, a representative sample of the error bars would be helpful.

21. Figure 9: perhaps consider adding a pictorial representation for the NOx cycle.

Congrats on a great submission. Good luck with revisions.

END OF REVIEW.

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