Atmos. Chem. Phys. Discuss., 10, C8219–C8226, 2010
www.atmos-chem-phys-discuss.net/10/C8219/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evidence for heterogeneous chlorine activation in the tropical UTLS" *by* M. von Hobe et al.

Anonymous Referee #3

Received and published: 4 October 2010

This paper presents airborne in situ observations of enhanced ClO in the tropical UTLS suggestive of chlorine activation on cirrus ice clouds. Standard model simulations are unable to reproduce the observed ClO, O3, and NO abundances. The manuscript is generally well written, and certainly the results will be of interest to the atmospheric science community. I do, however, have a number of substantive comments, described in detail below, that I would like to see addressed before the paper is published.

I have a few general commments. The first is that in the end I am not convinced that a data artifact would not provide a simpler and more compelling explanation for the apparent activation than the complicated series of model sensitivity tests needed to finally

match the observations. It may indeed be that these results call into question theoretical understanding of chlorine chemistry in the UTLS, but there are a few aspects of the measurements that have not been adequately explored (or at least described here). Another general comment is that the presentation is too often marred by assertions that are unsupported by the current text. In most cases this can be easily remedied by simply expanding the discussion a bit more. Finally, although the plots have been cleverly laid out and present information efficiently, many of the figures are extremely difficult to read at their current size. Although it is possible to zoom in the PDF file, the authors should bear in mind that many readers continue print out hardcopies of journal articles, and in their current configurations Figures 2, 5, and 6 are effectively illegible in a printed copy (and Figures 7 and 8 are also a little too small).

Specific substantive comments: ——————————

- p18064, L4-5: "While during most flights significant amounts of ClO (∼10-20 ppt) were present only in aged stratospheric air" – in fact, I do not think that this point was really made in the text as explicitly as it should be. It is asserted in the abstract and in the summary, but not given much attention in the text of the manuscript itself. There is one sentence in relation to Fig 3, but I think it could be highlighted more, and I think it would also be appropriate to discuss this issue in connection with Fig 4 (where the stratospheric points do not seem to have very high ClO/Cly ratios).

- p18064, L14-16: It might also be mentioned that the observed O3 abundances are not reproduced in the standard simulations.

- p18070, L13: ACE-FTS should be defined, and a general reference should be added (e.g., the overview paper by Bernath et al.).

- p18071, L1: It should be stated exactly how "tropospheric air" is being defined here (e.g., based on x(O3), etc).

- p18073, L18-22: First, it is stated that "Observed temperatures were significantly

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colder than ECMWF temperatures. This offset was subtracted ..." The offset should be quantified here. Surely the difference between the observed temperature and the analysis varied, so was a constant offset subtracted over the entire trajectory? Was the same offset used for all trajectories? How was this offset determined exactly, and is it consistent with other (published) estimates of uncertainties in the ECMWF temperatures? Second, 10 ppm of H2O seems quite high. What is this based on, the FISH measurements?

- p18074, L14: "a typical ice particle radius of 10 micron" – a reference for this "typical" value should be provided.

- p18075, L4-7: "ClO is expected to remain below ∼2 ppt in air masses with a significant tropospheric fraction (x(O3)<300 ppb) in agreement with a large number of ClO observations at or below the HALOX detection limit". The authors tend to focus on the highest ClO mixing ratios (20-40 ppt), which obviously are well above both the noise level of the data and the expected mixing ratios in tropospheric air. However, Fig 3 shows quite a large number of measurement points with O3 < 300 ppb but with ClO values of 5-10 ppt (during TROCCINOX) and 10-20 ppt (during SCOUT-O3). On p18068, L3, it is stated that HALOX can measure mixing ratios of only a few ppt with a precision of 10-50%. I am wondering whether the substantial number of points in the 5-10 ppt range are considered evidence of enhanced ClO, or whether the precision of the measurements is actually slightly worse than 50%, at least at these low ClO abundances.

- p18075, L22-23: "It is evident that most events of enhanced ClO are linked to either temperatures < 195 K ...". First, the significance of 195 K as a threshold here should be explained. Second, while I agree that the very highest ClO/Cly ratios tend to be clumped at T < 190 K, I note that there are quite a few dark red points up to 200 K, and clusters of orange points at 210 and even 225 K. So it is a bit of an exaggeration to say that most enhanced ClO events occur at Ts below 195 K, unless "enhancement" is specified to be ratios exceeding 0.5. Finally, I suggest minor rearranging of this

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paragraph: the sentence introducing Fig. 5 (L21) discusses the correlation with ozone, but the relevance of ozone is not made clear for several more sentences. I found this slightly jarring.

- p18076, L1-2: "but rapid and quantitative transport to the TTL seems unwarranted due to loss". First, what does "quantitative transport" mean? I would also suggest rewording this as: "but the assumption of rapid transport to the TTL seems unwarranted because of loss". Then in L2-4, it is stated: "neither observations nor trajectory calculations support direct transport of boundary layer air to the TTL". Please support this assertion by pointing directly to the observations that back it up and provide a bit more explanation. Similarly, in L12-13: "This conclusion is supported by the CLaMS simulation". Is this the CLaMS_CTM simulation? Can this be discerned from a figure (I don't think so)?

- p18076, L16-19: "Elevated ClO always [occurs] with low temperature and the presence of ice water as indicated by the elevated FISH total water mixing ratios and the presence of large particles – most likely ice – detected by the FSSP instrument". In my opinion this is definitely an overstatement of the situation for several reasons. First, I would consider values of more than 20 ppt to represent "elevated ClO", yet an instance of such enhanced ClO at the beginning of the flight track on 19 Nov is not highlighted, although this is possibly because FSSP and FISH data do not seem to be available at that time. Other instances of slightly elevated ClO ($\sim$10-15 ppt) at both the beginning and end of the flight again raise the question, posed earlier, of whether these values constitute "enhancement". Second, temperature does not seem particularly low to me, especially during the highlighted regions on the 30 Nov flight. Third, H2O is also not strikingly high on either 19 Nov or parts of the 30 Nov flight, at least compared to some other flight segments. Finally, FSSP number densities are certainly not enhanced on two of the three highlighted flight portions on 30 Nov.

- p18076, L19-21: "As shown in the lower panels of Fig. 6, the distribution of water vapour around the flight track – estimated using CLaMS CTM – suggests highest ClO

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levels near the top of cirrus clouds". I'm sorry, but I am confused by Fig. 6. (I note other more cosmetic objections to Fig. 6 elsewhere.) I don't quite understand what the color contours show in the middle and lower panels. I assumed that the middle panel contours show simulated IWC vs potential temperature, but then I do not understand the (unlabelled) color bar. If it is indeed IWC, then I don't understand the units. Nor do I understand the statement about "the distribution of *water vapor* [not IWC] around the flight track". Moreover, the contours seem unnecessary to make the point about high ClO near the top of cirrus clouds, which seems to rely only on the highlighted grey bar in the upper panels lining up with where the magenta overlay coincides with the white contour showing predicted cirrus occurrence. I further assumed that the lower panels show periods along the 5-day back trajectories (14-18 Nov) calculated from each point along the flight track during which cirrus clouds were simulated to occur. But again I am mystified by the color bar.

- p18076, L21-22: "Interestingly, the observations on 30 November were made in darkness (SZA>100), where significant amounts of ClO are unexpected"!!! I am afraid that this is more than interesting, and it demands some sort of explanation. Unless the temperatures were quite high (which they don't appear to have been), then the activated chlorine should have been in the form of Cl2O2, not ClO, at night. In fact I am frankly surprised that the authors have chosen to highlight this set of observations, and it again makes me wonder about the quality of the data. Can the authors be certain that these apparently large ClO mixing ratios are not measurement artifacts? It would actually be helpful to have some kind of statistics to indicate how many instances of apparently enhanced ClO were actually observed during these campaigns. Were all of the other examples at lower SZA? Are the 30 Nov data some of the highest ClO abundances observed? Were other high-ClO points, if any, less correlated with T and ice?

- p18076, L26-27: "Using the observed mixing ratios of ozone, NOy, and H2O, the simulation did not reproduce the observed ClO mixing ratios". It would be alot easier to tell this (and about the NOx discussed later on p18081), if the data were shown –

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could be just a point at time = 0 in the relevant panels of Figs 7 and 8.

- p18077, L3-4: "the runs with 200 ppb O3, CLaMS_BT predicts ClO to be present in significant amounts during night-time". The nighttime ClO mixing ratios in this simulation may be "significant", but they are still < 10 ppt.

- p18079, L3-4 and L15-16: Both of these sentences make assertions about the results of the simulations that are not supported by anything shown in the paper. At the very least the authors need to state "(not shown)".

- p18081, L11-13: "A combination of all changes with the assumption of 5 ppt Bry would result in full chlorine activation at 50 ppb O3". This may be true, but it seems to me that the authors have gone through some fairly extreme gymnastics to get there. There should be some discussion on how likely they think it is that all of these changes might be reflective of reality. Occam's razor springs to mind – rather than having to invoke a whole series of changes that push the boundaries of accepted limits, might it not just come down to an artifact in the data?

Typos and other minor wording comments: ——————————————

- p18064, L8: "concurs" is not really the right word. I suggest "are associated with"

- p18066, L6: I'm not sure that there is a universal definition of "inner tropics", so you might specify exactly what is meant, just as "midlats" was defined; L10: "exist and have been"; L14-15: only those words that actually go into constructing the SCOUT acronym should be capitalized

- p18067, L18: add comma after "added"

- p18068, L4: "in the same order"–> "on the same order"; L20: should be "subisokinetic"

- p18069, L6-8: "As is the FISH instrument, it is based on the ... the inlet minimizes the influence of the condensed ..."; L12: delete the comma after "parameters"; L19: add

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comma after "block"; L22: it might be better to say "number of non-volatile particles"; L23: "2.7 to 31"

- p18070, L16-17: add commas after "high" and "deviation)"; L26: add comma after "1993)" and change comma after "(O3)" to a period

- p18072, L21: delete "being"

- p18075, L3: add "dark" to "grey shading"; L12: "suggesting heterogeneous reactions causing" –> "suggesting that heterogeneous reactions caused"; L29: "100" –> "hundred"

- p18076, L7: add "(Figure 3)" after "TROCCINOX"; L10: add a comma after "(Fig 2a)"; L16: "concurs" –> "occurs"

- p18077, L3: add "(green)" after "200 ppb O3"; L7: "light" –> "sunlight"; L9: delete comma after "(chain 1)

- p18078, L2: "following" –> "subsequent"; also add a comma after "reaction"; L6: "(9)" –> "(R9)"; L17: "(10)" –> "(R10)"; L19: it would be good to explain the difference between the "x" and "c" notation

- p18080, L16: "factor 3" –> "factor of 3"; L20: "activation on various" –> "activation to various"

- p18081, L10-11: "correspond to higher assumptions for Bry" –> "correspond to assumptions of larger Bry"

- p18082, L9: "depend" –> "depends"; L15: "conditions at" –> "conditions under"

- p18088, L6: add comma and space in "Pasadena06-2"; L27: "occurence" –> "occurrence"

- p18091, L2 of caption: add "(green)" after "TROCCINOX" and "(red)" after "SCOUT-O3". This figure is too small.

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- p18094, last line of caption: add "(symbol size)" at end. This figure is *way* too small.

- p18095: what is "zeta" on the y-axis of middle panels? This figure is too small.

- p18098: probably should state in the caption that green denotes heterogeneous reactions. Why are the arrows from HOCl and ClONO2 not actually pointing at Cl2?

- p18099, L2 of caption: "Ozone" –> "ozone"

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 18063, 2010.