

Dear Jens-Uwe and co-authors,

this is an interesting paper on an important topic which has been discussed in the stratospheric CTM community for some time now, and I recommend it for publication. Even though this significant HCl discrepancy between models and observations during the onset of chlorine activation does not have a large impact on the overall ozone loss, it may be one of the last remaining gaps in our understanding of stratospheric chemistry and microphysics.

Your explanation based on the decomposition of particulate HNO₃ sounds promising to me, and the paper is well structured and written. There are however serious issues with the interpretation of Figure 7 and 8 in section 5 in my opinion (see major comments) and the conclusions drawn from that are probably not valid.

In addition, while I found the paper very detailed and providing much insight on some aspects, in some parts of the paper I miss information that should be in there (literature, other models, other possible explanations), and partly related to this, I don't think that the discussion in the paper is always well balanced. I would recommend to broaden the scope of the paper a little and to summarize what has been discussed so far. See more details in the major comments below.

Ingo Wohltmann

Major comments

- I was a little bit surprised that it is not mentioned in the abstract, introduction or conclusion, that there are also other models (apart from the models of the authors) which show the same behaviour (i.e. ATLAS and MIMOSA-CHIM). In addition, some of the relevant literature is not cited. I acknowledge that my Wohltmann et al. (2017) paper is cited later in the detailed discussion, but some other papers are missing completely. I would suggest to cite the following papers in the introduction:
 - Brakebusch et al., *J. Geophys. Res.*, 118, 2673–2688, 2013 (SD-WACCM).
 - Solomon et al., *J. Geophys. Res.*, 120, 7958–7974, 2015 (SD-WACCM). This is only cited in the model description so far.
 - Kuttippurath et al., *Atmos. Chem. Phys.*, 10385–10397, 2015 (MIMOSA-CHIM).
 - Cite Wohltmann et al. (2017) not only in the discussion, but also in the introduction (ATLAS).
 - It may also make sense to cite Santee et al. (2008), *J. Geophys. Res.*, 113, doi:10.1029/2007JD009057 (SLIMCAT), since it shows a discrepancy of opposite sign that may be related to numerical diffusion.

In fact, the HCl discrepancy seems to be present in all model publications, who have ever looked at HCl mixing ratios in the time period of the onset

of activation in the polar vortex. To me, this strongly suggests that this problem is present in all stratospheric CTMs, even in those who have not published anything on this topic so far. I think it is important to stress this right in the abstract or introduction.

- In a similar direction: Given that this is the first publication which explicitly deals with this topic and given that this topic has been discussed in the stratospheric CTM community for several years, I would expect that this paper gives a better overview over the processes relevant to resolve the discrepancy, which have been discussed so far. These are not restricted to the possible explanations you discuss here in more detail. While you mention some shortly, and some may be easy to discard, I think it would greatly add to the value of the paper, if you would discuss at least some of the following in more detail (following my list in Wohltmann et al., 2017):
 - Initial amount of ClONO₂ compared to HCl (how well do we know that?) (e.g. Brakebusch et al., 2013, Wegner, 2013)
 - Over- or underestimation of transport over the vortex edge (e.g. Solomon et al., 2015)
 - Take-up and sedimentation of HCl in cloud particles (Wegner, 2013)
 - Unknown reactions (Wohltmann et al., 2017)
 - An underestimation of the solubility of HCl (the following two bullets are partly related to this) (e.g. Wegner, 2013, Brakebusch et al., 2013, Wohltmann et al., 2017)
 - A temperature bias in the meteorological data driving the model (e.g. Brakebusch et al., 2013, Solomon, et al., 2015)
 - A water vapour bias in the model

This is also relevant since the discrepancy will not necessarily have only one reason, but may be caused by a combination of the above. Most of these have already been mentioned in the publications I recommend in the first major comment, and it would be a good idea to summarize the discussion here.

- You discard an underestimation of the HCl solubility as an explanation for the discrepancy all too easily in my opinion (which is also related to issues with the interpretation of your Figure 7, see next major comment). My results show that applying a correction to the solubility greatly helps to bring the MLS and model results in better agreement (see Figures 1 and 2 of this reply, look at the mean running averages). It does not seem to me that your “best explanation” (decomposition of particulate HNO₃ with a fixed rate) performs significantly better or that there would be more evidence into this direction. A more balanced discussion would be appropriate here. You certainly do not need to share my opinion, but more discussion of the solubility approach is needed here.

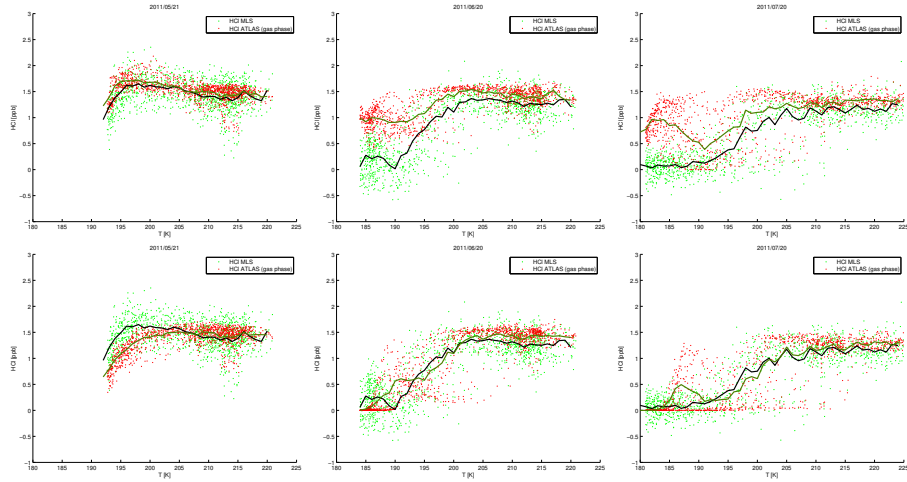


Figure 1: MLS HCl and ATLAS HCl (gas phase) at 46 hPa (one of the MLS measurement levels) as a function of temperature, to compare with Figure 7 of the paper. Top row: Without solubility correction. Bottom row: With solubility correction as applied in Wohltmann et al. (2017). Columns are different dates (21.5.2011, 20.6.2011, 20.7.2011). Solid lines are moving averages (MLS black, ATLAS dark green). All measurements south of 30 deg S are shown.

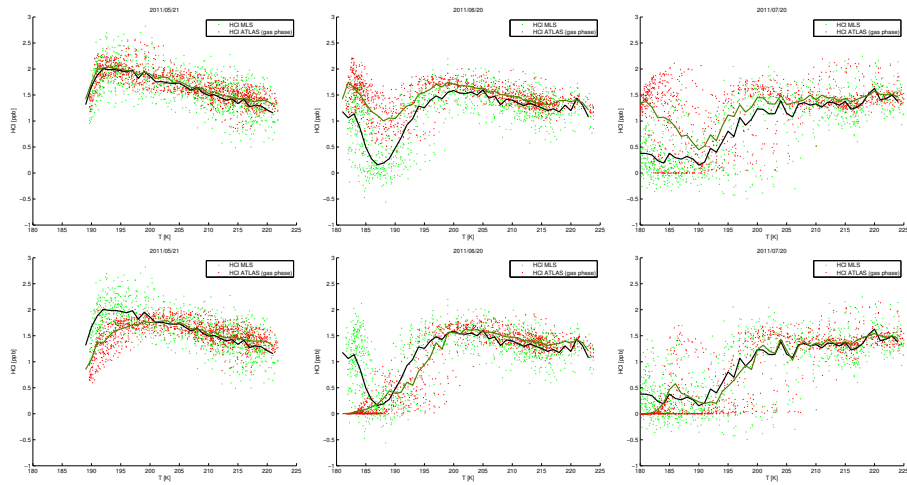


Figure 2: Same as above, but for 31 hPa.

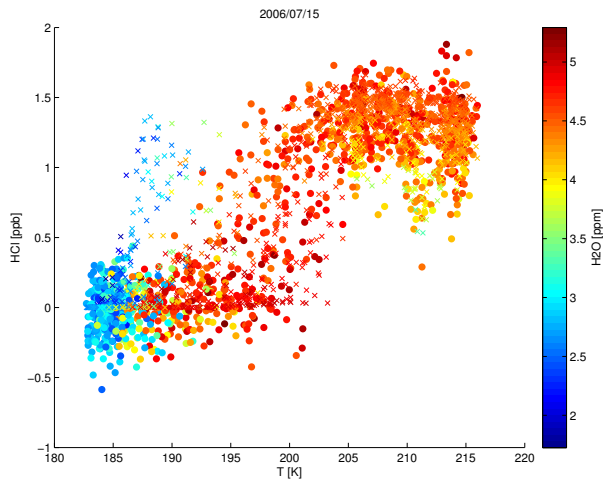


Figure 3: Same as in Figs. 1 and 2 for 15.7.2006 at 46 hPa, color coded by water vapor mixing ratio (crosses for modelled HCl and H₂O for ATLAS, dots measured for MLS).

I am the first to acknowledge that the solubility approach is certainly not “the” explanation or the only cause of the discrepancy and that it has several serious issues. For example, while the running averages (as a function of temperature) agree surprisingly well after application of my 5 K correction (Figs. 1 and 2), individual points show large deviations.

To illustrate a particularly bad example, I show data from 15 July 2006 in Figure 3. It is evident that under dehydrified conditions under very cold temperatures, the solubility approach does a very bad job. This is related to the fact that the solubility decreases with decreasing water vapor. However, in the MLS data, very low HCl levels are maintained under dehydrified conditions, excluding the solubility approach as an explanation under dehydrified conditions with the current parameterization.

In addition, the 5 K shift is really huge and not compatible with the Luo et al. (1995) parameterization that we probably all use in our models. The solubility parameterization is however not really my area of expertise, and it is difficult to judge for me in how far a different parameterization would be possible and be of help here. Maybe it would be an idea to both introduce a shift in temperature and in water vapor?

I think it would be important to discuss the things I mention in the above paragraphs in a little more detail to get a more balanced discussion.

- I think there are serious issues in the interpretation of your Figure 7 and 8 in section 5. I don’t think you can draw the conclusions about the tem-

perature dependency and dependency on sunlight of the HCl discrepancy that you draw here and that this section has to be rewritten.

Small changes to the altitude or the date of the figure produce results that can be interpreted completely differently. As an example, I have shown results to compare with your Figure 7 for 46 hPa (my Figure 1) and 31 hPa (my Figure 2) (the 46 hPa and 31 hPa levels are measurement levels of MLS roughly enclosing your 500 K level). These show a completely different temperature dependency for the MLS data for 20.6.2011, which is related to the “tongue” of high HCl visible in Figure 2 of your paper. While the 46 hPa data show a decrease of MLS HCl with decreasing temperature (upper row, second column, Figure 1), the 31 hPa data show an increase. Similar differences in interpretation are found when looking at another date (20.7.2011, right column).

Apart from this vulnerability to small changes, I think that this kind of figure is notoriously difficult to interpret, if a) there is more than one process causing the discrepancy, and b) the processes changing HCl have a memory. I.e., the figure is only easy to interpret if HCl is determined instantaneously by a single process.

The same issues apply to your Figure 8. I can easily produce a figure, where with increasing sunlight time, the discrepancy does not increase (Figure 4 of this review).

But that is even not the main problem with your Figure 8. When I try to reproduce your Figure 8 with the 195 K constraint, I get much lower sunlight hours than you, and no apparent dependency of the discrepancy on sunlight hours below 195 K (my Figure 4, left). When I however just calculate the total sunlight hours (right), the figure looks more similar to your figure (note that I plotted all measurements south of 60 deg S, which explains the higher values for the sunlight hours). I have the impression that there may be a bug in the calculation of the values for your Figure 8, and that the 195 K constraint may be missing.

That may also explain why your Figure 7 and 8 look so similar, since temperature and sunlight hours are highly correlated if you skip the 195 K constraint (Figure 5 of this review).

- You spend quite some time to show that the process is dependent on sunlight in section 5. But your best explanation (6.3, decomposition of particulate HNO₃) is not dependent on sunlight. How does this fit together? This obviously requires some discussion in the paper. Maybe it is related to the issues in section 5.

Specific comments

- Page 1, line 9: Wouldn't it be better to speak of SD-WACCM (here and elsewhere) to make clear that you are using the specified dynamics version of WACCM here?

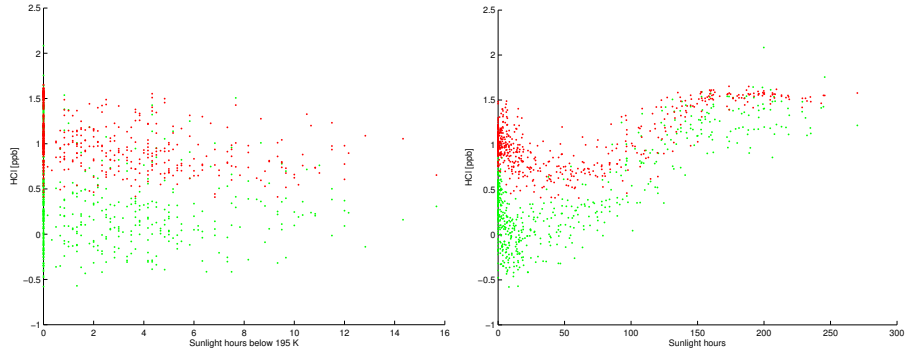


Figure 4: HCl as a function of sunlight hours below 195 K (left) and total sunlight hours (right), for 30 day back trajectories starting 20.6.2011 at the MLS measurement locations at 46 hPa south of 60 deg S for my uncorrected run, to compare with your Figure 8. MLS is green and ATLAS is red.

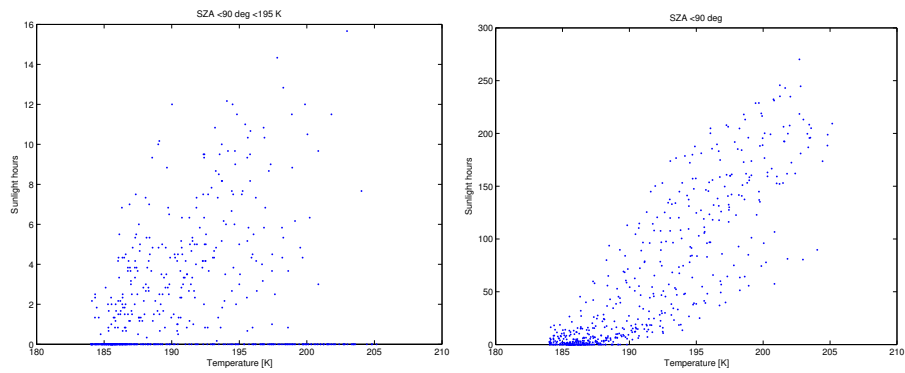


Figure 5: Sunlight hours below 195 K (left) and total sunlight hours (right) as a function of temperature at start for 30 day back trajectories starting 20.6.2011 at the MLS measurement locations at 46 hPa south of 60 deg S.

- Page 1, lines 16–17: Really? You discard this all too easily in my opinion, see major comment.
- Page 1, lines 20: As long as you don't know the processes that would lead to this HNO₃ decomposition, this is no better explanation than the solubility approach.
- Page 2, line 30–31: “not yet been reported”. You need to change the formulation. In the next sentence, you show that this is not true and that it has been reported in Wegner et al. (and later in Brakebusch et al., Solomon et al., etc.). Maybe just keep the next sentence and delete this one?
- Sections 2.1–2.3: I would suggest to describe the different heterogenous schemes (microphysics/chemistry/sedimentation) in some more detail here (as long as it is important for HCl) and to contrast the schemes of the different models to point out in which respect they are different (or identical). That may also be helpful to understand differences in HCl between the models better.
- Page 7, lines 13–15: I find the tone of this discussion unnecessarily negative. I am certainly not a completely neutral reviewer with respect to my model, but I think a neutral reviewer would have the same comment. First, you write that I did not “find an explanation”. But the same is true for this paper. Both of us examined several possibilities for explanations of the discrepancy, and both of us did not find a “final” explanation that would resolve the issue completely. Then, your “best” explanation is as “empirical” as mine. The text here and the following discussion in the next sections however sounds as if my explanation would be empirical and arbitrary, while this is not the case for your “best” explanation. Finally, the addition “but without further evidence why that could be.” is completely unnecessary. Please delete this part. I discussed the pros and cons of different explanations on more than two pages, even though I was restricted to keep this short for several reasons. You have very similar problems in your paper (“...the exact mechanism needs to be clarified ...”)

I would suggest a more balanced discussion here, at least that it is mentioned that you have similar problems to the ones that I faced in my publication. A more balanced discussion would also include to mention ATLAS (and the Kuttippurath paper for MIMOSA-CHIM) in the introduction and/or conclusions.

- Page 8, line 5: You write “For this example trajectory”. Does that mean that there are other cases which look worse? Or is the trajectory representative?
- Page 9, line 8: It is also worth mentioning that it is also strongly dependent on water vapor.

- Page 9, lines 12–15: See major comment. I don’t think you can draw this conclusion.
- Figure 7: It is interesting that both the CLaMS and the “uncorrected” ATLAS HCl values seem to increase with decreasing temperature. As I said in the major comment, I would not overinterpret a plot like Figure 7, but maybe that hints to something?
- Page 9, line 16–24, Figure 8: See major comment. I don’t think you can draw this conclusion.
- Page 9, line 29 and Figure 9: I can’t follow you here that there is a correlation between $d\text{HCl}/dt$ and PSC occurrence based on Figure 9. While there are clear minima in $d\text{HCl}/dt$, the PSC occurrence oscillates somewhere around 0.6 all the time. In fact, there are e.g. higher values for PSC occurrence in end of May than during the periods of low $d\text{HCl}/dt$ values later in June and July. It is also not clear to me what the discussion in lines 25–35 is supposed to tell me. I have the impression that this needs to be rephrased.
- Section 6.3: This looks quite promising and very interesting. I would however make more clear somewhere in the paper that there may be other explanations, which possibly work equally well, and which are not discussed in this manuscript. In particular, while your argumentation leading to this explanation is quite logical and sound, the weak point is your assumption of a rather arbitrary fixed rate here, where you don’t really know where it comes from. That is quite comparable to the situation with my ad hoc assumption of a 5 K shift in HCl solubility, where I don’t really know where it comes from.
- Section 6.3: How does the simulated HNO_3 compare to MLS HNO_3 , with the decomposition switched on and off? A better agreement when switching on the decomposition would strengthen your point.
- Page 12, line 10: Is the rate of 10^{-7}s^{-1} compatible with the amount of galactic cosmic rays (or secondary electrons with the right energy)? Or is this just a value empirically chosen to get the best fit with the HCl measurements? That should be stated here.

Technical corrections

- Page 9, line 22: “in sunlight”?
- Page 11, line 4: Change “Evidenc” to “Evidence”
- Page 11, lines 32–33: Change “a similar processes” to “a similar process”