Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "On the discrepancy of HCl processing in the dark polar vortices" *by* Jens-Uwe Grooß et al.

Jens-Uwe Grooß et al.

j.-u.grooss@fz-juelich.de

We thank Alexander D. James for the comment on our manuscript. Please note our answer below. The comments are repeated indented and *in italic letters* followed by our answers.

> *The authors present a useful summary, and thought-provoking new ideas, relating to a relatively well-known problem in stratospheric chemistry. This is likely to provoke future research and certainly merits publication following some revision.*

We thank for this valuation. Even though that seems to be a relatively well-known problem in stratospheric chemistry, it has not been properly documented in the scien-

C1

tific literature, which is the purpose of this manuscript.

> *The reference to the "dark polar vortex" in the title seems misleading given that the authors show an apparent correlation of the HCl discrepancy to hours of sunlight.*

This is a valid point. From our Fig. 8, it seems that the missing process needs sunlight, but we are looking at the vortex area with very little sunlight and the observations are mostly in the dark. We therefore changed the title of our manuscript to "On the discrepancy of HCl processing in the core of the wintertime polar vortices"

> *The reviews presented in RC1 and RC2 detail a number of additional processes which should be discussed in the text. In particular the paper lacks a discussion of the possible role of solid PSC. The loss of HCl is known to proceed rather differently on nitric acid hydrate (NAX) or ice surfaces compared to liquid PSCs (Chu et al., 1993). Hoyle et al. (2013) recently showed a good agreement between CLAMS and CALIPSO data on PSC type when a heterogeneous nucleation scheme was implemented, leading to a sharp onset in NAX nucleation below 195 K. In James et al. (2018) we then showed, based a study in our laboratory, that such heterogeneous nucleation can be caused by meteoric smoke or fragmented meteoroids, and can occur at temperatures as high as 197 K for typical stratospheric abundances of HNO_3, H_2SO_4 and H_2O.*

First of all we should note that we show that the problem of a missing HCl loss occurs in the models, because there is no reaction partner for HCl to react with as both the mixing ratios of $ClONO_2$ and HOCl are close to zero. The main problem is therefore not the available PSC surface area or the PSC type but rather likely a missing process to re-create $ClONO_2$ or HOCl. Therefore the PSC nucleation process is not a central issue of this paper.

C2

The CLaMS simulations do include a parametrisation of NAT and ice nucleation on likely meteoritic particles based on Hoyle et al. (2013) and Engel et al. (2013). The discussion on the PSC nucleation parametrisation has been kept rather short, since it is discussed by Grooß et al. (2014) for NAT and Tritscher et al. (ACPD, 2018) for ice in detail. This manuscript contains the description of the PSC nucleation parametrisation and a detailed comparison of PSC types and distribution of this CLaMS model setup. As the focus of this paper is on the missing HCl depletion, we feel that we should not repeat this documentation here.

> In figure 7 of the current text, the discrepancy is shown not to relate to temperatures below 194 K. I would like to make several points about this approach. Firstly, there is not only a lack of correlation between the model and observations, but in fact the general trend of HCl concentrations is rather different. The model shows a gradual increase in HCl at lower temperatures, whereas the observations show a significant increase below 186 K. This temperature is consistent with the formation of water ice PSC. It would also be informative for the reader if data were included to higher temperatures, to include the formation of possible NAX between 197 and 194 K.

We cannot completely follow these arguments. We did choose this specific subset of MLS observation points in potential temperature, equivalent latitude and time such that they represent the ongoing HCl depletion to be present both in the model and data. The mentioned increase in the MLS data below 186 K is in fact a "missing decrease" as the observations on this level are unperturbed HCl mixing ratios of about 2 ppbv before. So, if anything, the correlation with temperature alone would tell us about a process not taking place in the presence of ice.

Further, we simply plotted all available data of the chosen subset in the vortex core. There are no warmer observation points present in this specific subset. The idea of this plot was only to exclude the possibility of HCl uptake into liquid (or solid) particles. We do not see the largest discrepancy and the lowest gasphase HCl observations at

the lowest temperatures, which would be the case, if the missing process would be the uptake of HCl into any kind of particles. As also pointed out by the reviewer #1 this kind of figure should only give a hint, but must not be over-interpreted.

> In producing Figure 8 (setting to one side the concerns raised by the reviewers), a cut-off temperature of 195 K is used. This is reasonable if the growth of liquid PSC through deposition of H_2O is the determining factor; however, it is known that significant nucleation of NAX can occur above 195 K (Peter and Grooß, 2012). A more appropriate approach might be to examine the difference between the nucleation scheme used in each model (presumably the same as the Hoyle et al. (2013), Carslaw et al. (2002) and Brakebusch et al. (2013) schemes for CLAMS, SLIM-CAT and WACCM respectively) and the more recent literature. In James et al. (2018) we showed that different parameterisations of nucleation give rather different results in terms of particle concentrations and therefore surface area. A simple and informative experiment would be to correlate the HCl discrepancy to the difference between the onset of nucleation (e.g. time spent between 197 and 195 K for models using a constant volume nucleation rate, see Figure 6 in James et al. (2018)). Since MIPAS data are used extensively another obvious approach would be to relate the HCl (or $ClONO_2$) discrepancy to the data on PSC type which MIPAS provides.

> It is not possible given the present text to assess whether the presence of solid PSC could explain the discrepancies; however, with the inclusion of the references mentioned above and the subsequent suggestions (see above), this could prove an important process contributing to the HCl discrepancy.

From our analysis, there seems to be a hint (not a proof) that PSCs may be involved in the potentially missing process. It may well be, that the missing link involves solid PSCs. In fact, we suggest solid NAT in our hypothetical simulation "NAT decomp". However, it is clear from our study, that the standard heterogeneous chemistry on any

of the PSC particles cannot explain the observed HCl depletion, since HCl lacks a reaction partner in the models.

To strengthen our arguments, that CLaMS is able to simulate the basic properties and extent of PSCs, we add also the PSC observation fraction of CLaMS into the lowest panel of Fig. 9.

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