**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Temperature thresholds for polar stratospheric ozone loss" by K. Drdla and R. Müller

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General comments

We thank Susan Solomon very much for her comments. It is good to have her view on the issues and this has helped us clarifying what we want to say.

However, she has also raised several concerns about the paper as it stands. In our view, these concerns regard mostly points that the paper is not trying to make to extent assumed in the comment. Most importantly, it is a misunderstanding that the paper is trying to argue for "major changes in the way people do large scale modelling" or that reaction on cold binary aerosol is the only process occurring in the 'real word' or the

only process relevant for subsequent ozone loss. We believe that we have identified the points which caused the misunderstanding and hope that the revised version of the paper is much clearer on these points.

The paper is focussing on the onset of heterogeneous chlorine activation mainly through reaction

$$HCl + ClONO_2 \longrightarrow Cl_2 + HNO_3 \quad R1 \qquad (1)$$
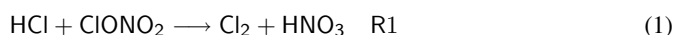
The paper makes the point that the threshold temperature T_{ACL} should be used as parameterization for the onset of chlorine activation in place of T_{NAT} and that cold liquid binary aerosol particles are the particles which, upon cooling in polar winter, first provide surfaces with substantial reactivity of heterogeneous chlorine activation.

To clarify these points, we have added this sentence to the abstract: "Considering T_{ACL} as a proxy for chlorine activation can be no substitute for a detailed model calculation and polar ozone loss is influenced by other factors beyond the initial chlorine activation". There is also a more detailed explanation in the beginning of the introduction: "Heterogeneous reactions are important for the magnitude of polar ozone loss during three phases in polar winter and spring. First, the initial rapid activation, when temperatures in polar winter fall below the threshold that allows heterogeneous chlorine activation to be effective, second, the slower activation of the HCl that remains after the initial activation and, finally, the period in late winter and spring when heterogeneous reactions compete with rapid gas-phase deactivation reactions for the maintenance of high levels of active chlorine".

We respond to the comments in detail below.

Response in detail

1. Uncertainty in kinetic parameters: In the paper, we use the parameterization by Shi et al. (2001) for the reaction R1 on cold liquid sulfuric acid aerosol, which is the study put forward in the current JPL evaluation (Sander et al., 2006), although no clear cut recommendation is given. Using the work of Hanson (1998) instead, leads to very similar activation time scales for temperatures between 192–195 K. The current JPL recommendation (Sander et al., 2006, Table 5-2) for R1 on NAT surfaces is a constant γ-value of 0.2 (and similarly for R2 and R3). In Fig. 1 of the paper we use both the constant JPL recommended γ-values and temperature dependent γ-values. We agree with the comment that there is considerable uncertainty in the temperature dependence of the γ-values and that in Fig. 1 the lower limit scheme for NAT reactivity (Carslaw et al., 1997; Carslaw and Peter, 1997) based on the measurements by Abbatt and Molina (1992) is used. This is now clearly stated in the paper. We also agree with the statement that no study to date has reconciled the different laboratory studies. A similar Figure to Fig. 1 has been published by Dameris et al. (2007), who used the upper limit scheme based on the measurements by Hanson and Ravishankara (1993) for the NAT reactivity and obtained the same basic result, namely that the time scale for heterogeneous chlorine activation of a typical NAT cloud is much longer than that on liquid aerosol particles. In a recent study (Wegner et al., 2011), a detailed comparison of the time scales for heterogeneous chlorine activation through reaction R1 and R2 is presented, corroborating the conclusion that at 192 K reactivities on cold liquid aerosol exceed those on NAT surfaces even if the the upper limit scheme based on the measurements by Hanson and Ravishankara (1993) for the NAT reactivity is employed.

   As suggested the discussion of this point has been extended. The relevant section now reads: "... Carslaw and Peter (1997) found that the laboratory measurements by Abbatt and Molina (1992) and by Hanson and Ravishankara (1993)

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   lead to very different reactive uptake coefficients for Reaction (R1) (up to factors of 50 to 100, Carslaw and Peter, 1997; WMO, 1999). Following Carslaw et al. (1997) we suggest considering two schemes for Reactions R1–R3 on NAT particles, one based on the measurements by Hanson and Ravishankara (1993) as an upper limit, and one based on an extrapolation of the measurements by Abbatt and Molina (1992) as the lower limit. Incorporating this humidity dependence (Carslaw and Peter, 1997), adopting the lower limit scheme provided by Carslaw and Peter (1997) (based on the measurements by Abbatt and Molina, 1992) [...] A similar Figure to Fig. 1 was published by Dameris et al. (2007), who used the upper limit scheme based on the measurements by Hanson and Ravishankara (1993) for the NAT reactivity and obtained the same basic result, namely that the time scale for heterogeneous chlorine activation of a typical NAT cloud is much longer than that on liquid aerosol particles. In a recent study (Wegner et al., 2011), a detailed comparison of the time scales for heterogeneous chlorine activation through reaction R1 and R2 is presented, corroborating the conclusion that at 192 K reactivities on cold liquid aerosol exceed those on NAT surfaces even if the the upper limit scheme based on the measurements by Hanson and Ravishankara (1993) for the NAT reactivity is employed".

2. Role of deactivation: The point of this paper is certainly not to say that "deactivation does not matter". We have to apologize for not being clear enough here. Clearly, deactivation (and thus denitrification) has an impact on the maintenance of high levels of active chlorine and thus on ozone loss. The paper was revised to make this point much clearer than in the submitted version, it is clearly stated now that heterogeneous reactions compete with rapid gas-phase deactivation reactions in late winter and spring (see also above). Regarding table S1, the main reason for the stronger Antarctic ozone loss is the longer period extending into spring available for ozone loss (1 November versus 10 March). Clearly, persistence of low temperatures and the resulting heterogeneous processing are

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required for continuing ozone loss. (See als point 4. below.)

3. The relevance of the meteorological variability from winter to winter and temperature uncertainties: We agree with the comment that for describing heterogeneous chlorine activation and polar ozone loss considering the variability from winter to winter is important and that uncertainties in the polar temperatures limit the confidence which one can have in the simulation of chlorine activation in a particular case. However, this in true independently of using T_{NAT} or T_{ACL} as the threshold for the onset of chlorine activation, isn't it? There are certainly circumstances in case studies where the temperature uncertainty does not allow conclusions to be made about the surfaces on which chlorine activation actually occurs in the real atmosphere. However, we argue that (independently of the uncertainties in stratospheric temperatures) describing the threshold temperature for chlorine activation based on the physico-chemical processes that actually occur (i.e., using T_{ACL}) is advantageous over using T_{NAT}.

4. Results for the Antarctic ozone hole for the year 2000: We agree with the comment that, in principle, for the Antarctic in the year 2000, inspite of an insufficient chlorine activation in a model study, ozone loss in October could be correctly described (as Antarctic ozone loss is saturated to a large extent in 2000). However, this is not the case for chlorine activation, which is the focus of Table S1 and the accompanying discussion. If the model predicted the right ozone loss for the wrong reason it would be obvious from the chlorine activation. Further, Table S1 makes the point that cold binaries are *not* sufficient on their own. In the LiqTACL case (cold binaries only) both chlorine activation and ozone loss (while still substantial) are significantly reduced.

   We understand from the review that this point needs to be discussed in more detail and have therefore (as also recommended in 8. and by the anonymous reviewer) moved table S1 with the accompanying discussion into the main body of the paper.

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   Moreover, as suggested in the comment, we have now included a much more extensive discussion of the work of Portmann et al. (1996). The respective section reads: "Portmann et al. (1996) investigated the interannual variability of Antarctic ozone loss and demonstrated that the variability and, in particular, the increases in Antarctic ozone depletion in the 1980s could only be reproduced by a model that included the observed interannual variation of stratospheric aerosol. Further, Portmann et al. (1996) found that the increase in stratospheric aerosol caused by the eruption of Mt. Pinatubo in 1991 primarily affected the vertical extent of the ozone hole in their simulations since the simulated ozone loss at the altitudes with the strongest loss was nearly complete, even when the volcanically enhanced aerosol was not considered."

5. Sensitivity to initial HCl and ClONO$_2$ abundances: In the model runs presented the assumed HCl/ClONO$_2$ ratio is 2/1 and we agree that this ratio determines the amount of active chlorine that is produced in the first activation step. Although there are now measurements available on the HCl/ClONO$_2$ ratio from the Microwave Limb Sounder (MLS) on Aura and the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) on SCISAT-1 (Santee et al., 2008) there is clearly some uncertainty in this quality. We discuss this issue now more explicitly in the paper. However, the improvement of using T_{ACL} in place of T_{NAT} for describing the threshold temperature for the onset of chlorine activation is not substantially affected by this uncertainty. Note (see also the discussion on Table S1 below) that we are not arguing that binary aerosol particles are doing the job (of chlorine activation) "alone".

6. Comparisons to observations: The paper focuses on the processes relevant for the onset of chlorine activation. The discussion is first based on laboratory studies of heterogeneous reactions of chlorine compounds. Model simulations using a heterogeneous chemistry scheme based on those laboratory studies are then used to derive the threshold temperature T_{ACL}. Tilmes et al. (2008) find that us-

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ing T_{ACL} in place of T_{NAT}, a better description of Arctic ozone loss emerges for volcanically perturbed conditions. We agree that the ultimate test will be to a comparison with a range of atmospheric observations of first chlorine activation and second ozone destruction. However, as also pointed out in Section 4 of the comment, not all conditions are well suited to discriminate between activation on particular surfaces. In a recent study Wegner et al. (2011) analyze a case where ClO was measured in a reactivation event in March 2005 that allows such a discrimination to a certain extent.

7. Sensitivity of the results to assumptions about PSC and CALIPSO results: An important point here is that the CALIPSO results (see Figure 2.13 in WMO (2011)) show that the area below T_{NAT} is clearly larger than the area covered by PSC (counting all types of PSC detectable by CALIPSO). This point is made now in the paper.

Pitts et al. (2010) find that 13% of the CALIPSO PSC observation between 2006–2010 fall into the a categorie (Mix 2-enh) of NAT particles with relatively high number density ($> 0.1 \mathrm{cm}^{-3}$) embedded in an STS cloud. In the extremely cold Arctic winter period in Januray 2010, there were significantly more observations of this type of PSC (and of ice PSCs) than before (Pitts et al., 2010). However, it is important to note that these observations were made at temperatures well below T_{NAT} and that the "NAT, Original" calculation assumed a even greater NAT concentration of $1 \mathrm{cm}^{-3}$. Further, the Mix 2-enh clouds are mixtures so that the chlorine reactivity is not a pure NAT reactivity but rather a mixture of STS and NAT reactivity. Finally, higher number density liquid/NAT mixtures, were primarily observed by CALIPSO downstream of wave ice clouds, where substantial chlorine activation has probably occurred. This effect should reduce the importance of the Mix 2-enh clouds for chlorine activation in general and in particular for the onset of activation. But in any case we agree that the CALIPSO results are important (Pitts et al., 2010) and have extended the discussion of this issue in the

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paper.

8. Tables S1 and S2: We agree with the points raised in this comment. However, apparently or presentation was confusing. This issue is hopefully rectified in the revised version of the paper (including the addition of references). First of all, this section and the Table S1 has been moved to the main text as suggested (Table S2 has been dropped as it does not add much information and might be confusing). We have also discussed uncertainties now and agree that table entries on the tens of a percent level is not appropriate – this has been changed.

We have now made clear in the text that all scenarios in Table S1 except FullPSC are meant to be sensitivity studies and not representations of what happens in the 'real world'. We certainly agree with the comments from the review that if "temperatures are cold enough long enough to drive enough chlorine activation in sunlight without much deactivation, ozone loss will be extensive regardless of what kind of particle does the activation" and that just "because binary aerosols could do the job alone doesn't mean that binary aerosols alone are what actually does the job in the real world". This point is now made explicitly in the section in question.

Further, the test suggested in the comment ("If a 'fullpsc' case had been done followed by a case with, e.g., ternaries only, [. . .] wouldn't the key results have been similar – but with activation deemed to occur on very different kinds of particles") is presented in Table S1 as the "Liquid" case. And, as suggested in the comment, the results are similar to the "FullPSC" case with now indeed the activation occurring only on the STS particles present. However, this provides no argument against using T_{ACL} in place of T_{NAT}. Furthermore, the importance of the rate of heterogeneous reactions for the maintenance of high levels of active chlorine into spring is evident in the different chlorine activation level in case "LiqBin" and "LiqTACL" addressing another important issue raised in this comment. Again, we have made changes throughout the text to get this message across much more

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clearly.

9. Does it matter?: It is a misunderstanding that the paper is trying to argue for major changes in the way people do large scale modelling. We hope that the revised version of the paper is much clearer on this point. What the paper is doing is arguing using T_{ACL} in place of T_{NAT} when parameterizing the onset of polar chlorine activation. The paper is not putting forward T_{ACL} as an alternative for a proper model calculation using temperature dependent gamma values and a supersaturation threshold; as stated in the abstract: "Considering T_{ACL} as a proxy for chlorine activation can be no substitute for a detailed model calculation...". The distinction between T_{ACL} and T_{NAT} does matter; not under all circumstances, but see Figures 3 and 4 (ACPD version) in the paper.

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