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# *Interactive comment on* "Liquid particle composition and heterogeneous reactions in a mountain wave Polar Stratospheric Cloud" *by* D. Lowe et al.

**Anonymous Referee #2**

Received and published: 14 October 2005

This manuscript describes model simulations of a liquid-phase leewave PSC that was measured over Scandinavia, in particular examining whether the liquid particles were at equilibrium, and the implications of their non-equilibrium composition. Model/measurement comparisons provide some evidence that the liquid particles were not in equilibrium. The most novel aspect of the manuscript is an analysis of whether chlorine activation is affected by the non-equilibrium composition, since chemistry models universally assume that the liquid aerosol is at equilibrium. However, the discussion of chlorine activation is the weakest part of the manuscript, providing little substantive evidence that non-equilibrium effects alter chlorine activation. Therefore, the manuscript ultimately presents little new science and is probably of marginal interest for the readers of ACP.

Most of the manuscript presents model/measurement comparisons of the $NO_y$ content of the measured PSC, providing some evidence that the PSC was not in equilibrium. However, the evidence is not conclusive: at times the equilibrium model provides a better match to the measurements, $NO_y$ measurements are missing in the middle of the PSC, optical counter measurements are completely absent, and questionable model initialization causes widespread disagreement with backscatter measurements. General evidence for non-equilibrium liquid-phase PSCs has previously been published, and the case study presented here does not provide any substantial new information on this topic.

The more innovative part of the manuscript purports to demonstrate that calculations of chlorine activation are sensitive to non-equilibrium effects, by comparing chlorine activation from equilibrium and non-equilibrium simulations. However, the resultant effect is only 15%. Given that chemistry models rarely even consider chlorine activation in leewave clouds, and the numerous sources of uncertainty inherent in any calculation of leewave-induced chlorine activation, a 15% effect seems inconsequential. A temperature change of 0.5 K would result in a larger change in ClO. Additionally, the analysis of chlorine activation presented in this manuscript has enough weaknesses that it is unclear whether even a 15% effect is likely: the model contains no gas-phase chemistry, the model results can not be compared to $ClO_x$ measurements, possible effects of $HNO_3$ weight percent are ignored, and this paper provides only a single, non-representative case study. Overall, a more careful and thorough analysis of non-equilibrium chlorine activation is needed to make this part of the paper relevant.

A central weakness of this manuscript is the case study chosen for analysis. Because of limited measurements and the fairly warm temperatures, this PSC event provides a poor case study for either liquid PSC composition or chlorine activation. The research would probably be more sucessful if based upon a different case study, or else upon

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some generic but representative examples. The necessary changes, however, would be so substantial that the manuscript would no longer resemble the current one. I therefore do not recommend publication of this manuscript.

**Specific Comments:**

abstract, l. 10: "in reasonable agreement with the measured $ClO_x$ concentrations" Since $Cl_2$ at nighttime will not be measured by the HALOX instrument, no conclusions can be made about whether there is model/measurement agreement; see comments below.

abstract, l. 11-13: "Equilibrium calculations commonly used in large scale CTMs ..." This conclusion is also at best weakly supported by the manuscript. Given that CTMs do not even simulate mountain wave events, assuming equilibrium composition has no effect on CTM chemistry. Even if CTMs were to simulate mountain wave events, this conclusion should be supported by a comparison of the impact of equilibrium compositions with some of the other uncertainties, such as estimating the occurrence of mountain waves, temperature, microphysics, heterogeneous reaction rates, etc.

p. 9548-9549: The introduction needs to provide a discussion of the composition of STS, in particular how non-equilibrium compositions can arise in lee wave events. Also useful would be an overview of the mechanisms by which non-equilibrium compositions could affect heterogeneous chemistry.

p. 9549, l. 3: "A notable omission...." Section 4.1 does not appear to describe any omissions from JPL02... what is this supposed omission?

p. 9549, l. 13-15: Chlorine activation within PSCs has previously been modeled, and references to this work should be included in this discussion. For example, Jaeglé et al. [1997], Kawa et al. [1997], Hanisco et al. [2002].

p. 9549, l. 17: Techniques besides just gas-phase compositions and lidar depolarization have been used to infer particle compositions, including condensed phase mass, size distributions, condensed phase $HNO_3$...

p. 9552, l. 24-26: Is MAS depolarization data available on this flight? Why isn't it used?

p. 9554, l. 11: Provide details on the flight solar zenith angle here.

p. 9554, l. 11-14: This discussion of the impact of ignoring the gas-phase reactions is incorrect. For the nighttime conditions which are stated to be present, no $ClONO_2$ production would occur. Furthermore, for the modeled conditions $ClONO_2$ production would have no effect on $ClO_x$ yield ($ClONO_2$ is never depleted).

p. 9554, l. 18-19: The water activity is only equivalent to the atmospheric conditions if the solution is in equilibrium. Given that this study is explicitly examining non-equilibrium effects, the correct value to use for the water activity is not immediately apparent. Is water assumed to be in equilibrium? Does this guarantee that the water activity is determined by the ambient conditions?

p. 9554, l. 22: Hanson only studied reactions R1 and R2.

p. 9555, l. 10-11: Again, given the focus on non-equilibrium conditions, the assumption that HCl is in equilibrium needs more discussion. Does gas-phase diffusion of HCl or $ClONO_2$ limit the reactivity? Is gas-phase diffusion taken into account?

p. 9555, l. 22-25: How are the wind speeds determined, both for the quasi-lagrangian trajectory and the isentropic ones? The wind speeds are as important as the temperatures in controlling the cooling rates.

p. 9556, l. 15-16: How is the aerosol simultaneously initialized to contain 0.5 ppbv $H_2SO_4$ and fit the specified size distribution? The specified size distribution only corresponds to about 0.17 ppbv $H_2SO_4$ (which happens to be a more reasonable value than 0.5). Furthermore, especially given that the later comparisons with MAS suggest that the model is being initialized with too much aerosol, a reference should be provided for these values.

p. 9556, l. 27-28: Are the HALOX values measurements from within the PSC, upwind of the PSC, or downwind of the PSC? Is $ClO_x$ calculated from ClO + 2 $Cl_2O_2$, both as measured by HALOX? Why is HOCl assumed to be 0 initially? If previous processing has already produced 300 ppt of $ClO_x$, HOCl will also be present (maybe 100 ppt), which will play an important role in chlorine activation via reaction R3. The HOCl evolution in Figure 12b is unrealistic given that HOCl is artificially initialized to 0.

p. 9558, l. 23-24: It is not obvious that the non-equilibrium calculations are an overall better match to the measurements than the equilibrium calculations. For times > 1 hr, the equilibrium calculation looks better than the non-equilibrium calculation. In the event at 0.75-1 hr, the non-equilibrium calculation looks good except that SIOUX measurements are missing for most of the event. Only by looking at the MAS data is it possible to infer that the non-equilibrium model is closer to the data in this event. Given that this comparison is central to the paper's conclusions, a glib statement that one model is better than the other is not sufficient. Also, given the importance of the MAS data it would be useful to show both the equilibrium and non-equilibrium calculations in comparison to the MAS data.

p. 9559, l. 4-15: Why is no explanation given of the model/measurement discrepancies after 1 hr? In particular in comparison to the equilibrium calculations, the poor behavior of the non-equilibrium model warrants explanation.

p. 9559, l. 28: "about 1.5 ppbv below" Is this supposed to be 0.15 ppbv?

p. 9560, l. 13-20: This a surprisingly brief paragraph given that it provides the only analysis of a key topic, namely chlorine activation. No overview is ever given of how and why the non-equilibrium model should yield different chlorine activation; the effect of $HNO_3$ weight percent is only mentioned later. The "comparison" with HALOX data provides no meaningful information. An assessment of chlorine activation needs to evaluate how $ClO_x$ levels change during the event, e.g. difference in $ClO_x$ after and before the PSC. Any constant contribution to $ClO_x$ during the PSC is presumably from

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previous processing and irrelevant. The statement that it is "not straightforward" to relate $Cl_2$ to measurements of $ClO_x$ is false: there is quite simply no relationship. $Cl_2$ is not detected by the HALOX instrument, and without any sunlight $Cl_2$ will not be converted to other, detectable, $ClO_x$ species. So based on the provided information, the HALOX measurement provides no validation or corroboration of the model calculations.

Figures 1 and 2: Couldn't these two figures be merged? Also, some indication of the Geophysica flight direction, in particular for the northern PSC event, would be helpful.

Figure 9a: Are gray crosses only shown for a subset of the model points (i.e. those with > 0.3 ppb $NO_y$)?

Figure 12: Why does this figure show so much data from before the PSC event (which probably includes daylight conditions that can not even be simulated by this model)? Why not just focus on the same time period as all the other plots? Why does the equilibrium model have so much less HOCl production than the non-equilibrium model, especially before the PSC when presumably the two models have nearly identical aerosol surface areas and compositions?

**Technical corrections:**

p. 9549, l. 23: "presence on" should be "presence of"

p. 9557, l. 3-4: "thus neither are our conclusions" This phrase does not make any sense.

p. 9552, l. 15: missing apostrophes in "instruments", "Geophysicas"

many acronyms are used in the paper, none of which are spelled out.

**References:**

Jaeglé et al., Evolution and stoichiometry of heterogeneous processing in the Antarctic stratosphere, JGR 102, 13235-13253, 1997.

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Kawa et al., Activation of chlorine in sulfate aerosol as inferred from aircraft observations, JGR 102, 3921-3933, 1997.

Hanisco et al., Quantifying the rate of heterogeneous processing in the Arctic polar vortex with in situ observations of OH, JGR 107, 8278, doi: 10.1029/2001JD000425, 2002.

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9547, 2005.