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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.

D. Lowe et al.

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1 General

We thank the referee for pointing out several deficiencies in our manuscript, and hope that the revised ms is clearer and more convincing. We do not agree with the referee’s analysis of the novel aspects of the paper: the paper reports the first measurements made in quasi-Lagrangian fashion in a mountain-wave PSC, and analyses those results using a state-of-the-art model that allows composition to vary across the aerosol population. We are not aware of any studies in the literature that are comparable to ours - see our response below (ref. p. 9549, l. 13-15) - and think that the manuscript

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Interactive Discussion

Discussion Paper

will be of interest to many readers of ACP. The referee criticises our choice of case study and the lack of data from an optical particle counter. Of course, one would prefer to have the perfect dataset from the perfect atmospheric event, but the reality of aircraft campaigns prevents this. We demonstrate in the manuscript (i) that the event is significant and worth investigation, (ii) that the measurements we do have are new and interesting, and (iii) that we can learn much from comparison of data and model. We do not agree that the difference in chlorine activation demonstrated in the paper is "inconsequential". The purpose of the EuPLEx campaign was to quantify ozone loss rates, and to do that one should know chlorine activation in an air parcel to better than 10 %. The fact that global models don't include mountain-wave PSCs is hardly a reason not to study them, nor to try and quantify their effects. As for the uncertainty in our heterogeneous reaction calculations - it is one of the main conclusions of the paper that the lack of lab data introduces a significant (previously unacknowledged) uncertainty into model results. The referee has, however, helped us enormously by asking us to reconsider our results for HOCl. This has revealed a bug in the coding of the reactions rates that we have rectified (see below). The comparison of chlorine activation between equilibrium and non-equilibrium models now shows a 10 % change (15 ppt) in chlorine at the end of the model runs. The conclusions of the study are unaffected by this change in the detailed model results. We stand by our statement that this study shows some important limitations in the use of equilibrium ternary-solution calculations in models of PSCs.

2 Specific points

The referee's comments are repeated in italics, below, and are followed by our responses.

abstract, l. 10: "in reasonable agreement with the measured ClOx concentrations"

Since Cl2 at nighttime will not be measured by the HALOX instrument, no conclusions can be made about whether there is model/measurement agreement This has been removed.

abstract, l. 11-13: "Equilibrium calculations commonly used in large scale CTMs ..." This conclusion is also at best weakly supported by the manuscriptĚ As the resolution of global models increases, smaller-scale features are resolved, including large gravity waves. These are already apparent in current versions of the ECMWF operational model.

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. A discussion of STS composition has been added to the introduction. "The speed at which this change in composition occurs is controlled by the condensation rates of the individual components; the condensation rates are themselves determined by the particle size and partial pressure of the component in the gas phase. Thus, while the H2O-content of the condensed-phase can reach equilibrium with the atmosphere within seconds, the condensed-phase HNO3-content can take from several minutes for smaller particles (0.1 μm) to several hours for the largest particles (2 μm). The limited uptake rate of HNO3 means that rapid temperature fluctuations, such as those occurring within mountain lee waves, can lead to droplets with highly non-equilibrium compositions (Meilinger et al., 1995)."

p. 9549, l. 3: "A notable omission...." Section 4.1 does not appear to describe any omissions from JPL02... what is this supposed omission? Section 4.1 makes it plain that we have no parameterisation for reactions R1-R3 in STS. This is a substantial problem in the modelling of the heterogeneous chemistry. Perhaps, on reflection, the word "omission" implies some deliberate act, when we meant simply to note a lack of a clear parameterisation, so we have amended the text on line 3 of p9549.

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]. The papers cited by the referee do not attempt a similar analysis to the one presented here. Jaeglé et al. and Kawa et al. both use trajectories ending at the aircraft flight-path. The Hanisco et al. paper uses steady-state analysis for OH. We have re-written the sentence to be more specific: i.e., models have not been compared with measurements along quasi-Lagrangian trajectories.

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 HNO3Ĕ We have re-phrased this sentence to explain that several methods for inferring particle composition existed prior to the direct measurements by mass spectrometry and condensed NOy.

p. 9552, l. 24-26: Is MAS depolarization data available on this flight? Why isn't it used? The MAS depolarisation data was available, but did not show any signal above background. We have inserted a sentence explaining this into the text.

p. 9554, l. 11: Provide details on the flight solar zenith angle here. We have added a sentence showing this.

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 ClONO2 production would occur. Furthermore, for the modeled conditions ClONO2 production would have no effect on ClOx yield (ClONO2 is never depleted). Agreed. We have removed the text discussing the production of ClONO2.

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 nonequilibrium 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? Because of the very different fluxes of water vapour and nitric acid to the droplets, the water is very close to equilibrium for the condensed mass of nitric and sulphuric acids (see, Meilinger et al., 1995 and Lowe et al., 2003), and it is this water activity that we use. The modelled condensed and vapour nitric acid concentrations are often very far from equilibrium. The MADVEC model calculates both the water and nitric acid fluxes explicitly. This behaviour is described in the new paragraph describing non-equilibrium STS that has been added to the Introduction.

p. 9554, l. 22: Hanson only studied reactions R1 and R2. We have corrected this typographical mistake.

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 ClONO2 limit the reactivity? Is gas-phase diffusion taken into account? We added HCl to the model as an explicitly modelled fourth component, and found that the dissolved HCl was always close to equilibrium. This is due to the rather low solubility of HCl. The effect of the depletion of HCl in the particle phase due to the reaction with ClONO2 is taken into account in the parameterisation of Shi et al.

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. As we state in Section 5.1, the trajectories are calculated from ECMWF and MM5 output. The wind speeds in the sections taken from the aircraft flight path are taken from measurements onboard the Geophysica. We don't take the difference between aircraft and wind directions into account; however the aircraft flew close to the wind direction in this section, as was planned.

p. 9556, l. 15-16: How is the aerosol simultaneously initialized to contain 0.5 ppbv H2SO4 and fit the specified size distribution? The specified size distribution only corresponds to about 0.17 ppbv H2SO4 (which happens to be a more reasonable value than 0.5). Furthermore, especially given that the later comparisons with MAS sug-

gest that the model is being initialized with too much aerosol, a reference should be provided for these values. Our apologies, we neglected to include all details for initialisation. The aerosol was initialised at 199.5 K and 58.12 mbar, at which the mode radius of the particle distribution is 0.065 ?m (rather than 0.067 in our paper) for a number density of 10 cm-3. We have corrected this paragraph to include these numbers. Our condensed sulphate loading may be somewhat high for this volcanically quiescent period. We have run tests with other sulphate loadings, and smaller loadings do produce less particle-NOy, but the substantial difference between equilibrium and MADVEC calculations remains.

p. 9556, l. 27-28: Are the HALOX values measurements from within the PSC, upwind of the PSC, or downwind of the PSC? Is ClOx calculated from ClO + 2 Cl2O2, both as measured by HALOX? Why is HOCl assumed to be 0 initially? If previous processing has already produced 300 ppt of ClOx, 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. We have re-written this paragraph to try and make it clearer. We agree with your point about our initialisation of HOCl at 0 pptv being unrealistic. We have now changed this to 100 pptv.

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. In terms of the root mean square difference between model and measurements, surely it is obvious that the non-equilibrium model fits the data better. We state in the paper that some observed features are not modelled well by the non-equilibrium model; we have added a sentence to say that - in some of these places - the equilibrium model fits the data more closely.

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 behaviour of the non-equilibrium model warrants explanation. See our answer to the point above.

p. 9559, l. 28: "about 1.5 ppbv below" Is this supposed to be 0.15 ppbv? We have corrected this typographical error.

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 HNO3 weight percent is only mentioned later. The "comparison" with HALOX data provides no meaningful information. An assessment of chlorine activation needs to evaluate how ClOx levels change during the event, e.g. difference in ClOx after and before the PSC. Any constant contribution to ClOx during the PSC is presumably from previous processing and irrelevant. The statement that it is "not straightforward" to relate Cl2 to measurements of ClOx is false: there is quite simply no relationship. Cl2 is not detected by the HALOX instrument, and without any sunlight Cl2 will not be converted to other, detectable, ClOx species. So based on the provided information, the HALOX measurement provides no validation or corroboration of the model calculations. The referee is referring to our discussion of Figure 12 on page 9561. We make it clear in the paragraph that it is the surface area differences between the equilibrium and non-equilibrium calculations that produce the difference in Clx production. We have added a clause to explain that the water activity calculated by the two models is very similar even though the nitric acid contents are different. We agree that nothing more can be done to compare our model results with measurements of ClOx; we had been

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initially more circumspect because we were not sure of the amount of diffuse light that might be present at these altitudes and zenith angles. We have re-worded the section to remove any implied comparison between the model results and the observations. The abstract, discussion, and conclusions are now consistent on this point.

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. We have made Figure 2 more useful by including solar zenith angle data on it.

Figure 9a: Are gray crosses only shown for a subset of the model points (i.e. those with > 0.3 ppb NOy)? Yes, our apologies, we omitted to explain in the caption that the grey crosses are a small sample of the model output around 0.84-0.98 hrs, and simply illustrate the effect of sampling the model aerosol in the same way as SIOUX samples the atmospheric aerosol. Explanatory text has been added to the caption.

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? Our apologies, the majority of the difference was due to an error in the parameterisation of the heterogeneous reactions in the equilibrium calculations - this has now been fixed. Following the referee's suggestion, we graph the results of the model run over the same time period as the other figures.

The technical corrections have been made. Some of the acronyms are in fact now best regarded as proper names (e.g. MADVEC, SIOUX, HALOX, VINTERSOL) - spelling out the original derivation of these does not add any information.

References

Meilinger, S. K., Koop, T., Luo, B. P., Huthwelker, T., Carslaw, K. S., Krieger, U., Crutzen, P. J., and Peter, T.: Size-dependent Stratospheric Droplet Composition in lee wave Temperature Fluctuations and their potential role in PSC Freezing, *Geophys. Res. Lett.*, **22**, 3031–3034, 1995.

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