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Interactive comment on "Lagrangian analysis of microphysical and chemical processes in the Antarctic stratosphere: a case study" *by* L. Di Liberto et al.

Anonymous Referee #3

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General Comments:

This paper describes a case study of polar stratospheric cloud (PSC) microphysical and chemical processes during the late winter in the Antarctic stratosphere. The study utilizes ground-based, balloon-borne, and satellite measurements of PSCs, temperature, and relevant gas species along with microphysical and chemical model calculations to examine the role of heterogeneous chemistry and denitrification on the depletion of ozone along air mass trajectories over a ten-day period during September 2008. The comprehensive study evaluates the relative role of nitric acid trihydrate (NAT) and liquid particles on heterogeneous chemistry and the role of denitrification on gas phase

chemistry in the lower stratospheric within the Antarctic vortex. Overall, the paper is well organized, clearly written, and the resulting conclusions appear reasonable given the constraints/assumptions of the somewhat limited case study. However, there are a number of concerns that should be addressed before publication in ACP; these are expanded on below.

My major concern is the estimate of condensed nitric acid used to initialize the microphysical and chemical models. Assuming a bimodal lognormal size distribution (small mode consisting of liquid sulfate aerosol or STS and large mode consisting of NAT), you calculate that ∼22 ppbv of HNO3 would be condensed on the NAT particles. Although you acknowledge that this may be an overestimate, you still use a value of 20 ppbv condensed HNO3 to initialize the models and consider this to be realistic. What are you basing this on? Can you cite a reference? I think this is at least a factor of 5 too large. By late winter, sedimentation/denitrification have reduced the total abundance of HNO3 within the vortex significantly. In regions outside of PSCs (i.e. no HNO3 in the condensed phase), Aura MLS observations indicate HNO3 values closer to 3-4 ppbv at this latitude and altitude in late winter. So where does this additional ∼17 ppbv HNO3 come from? How would such an overestimate of condensed HNO3 affect the model calculations? If you assume that this HNO3 has been redistributed to lower altitudes by the time the PSC evaporates, there should be a signature of renitrification at lower altitudes. Do you see any enhancement in HNO3 at lower altitudes in the MLS data? Is the magnitude of renitrification (if observed) consistent with the volume of condensed HNO3 that has been redistributed to these lower altitudes?

If my contention that the actual condensed nitric acid is likely no larger than 3-4 ppbv, then there clearly is an inconsistency between the measured size distribution and available nitric acid. This may be of similar nature as discussed by Molleker et al. (2014) and be related to the shape of the NAT particles, e.g. perhaps the particles are significantly aspherical. This of course would affect the calculated surface area which probably assumes spherical particles. In addition, the estimated sedimentation is dependent on particle shape, so sedimentation rates may be inaccurate. Can you discuss how these potential discrepancies would impact your analyses and conclusions? In the end, you conclude that processing on NAT is not important anyway, so maybe this doesn't matter for heterogeneous chemistry, but the results would be more convincing if appropriate values of condensed NAT were used.

Although only briefly mentioned in the paper, the MLS and MIPAS instruments have very coarse horizontal resolutions (hundreds of kilometers), which will tend to smear out localized effects of denitrification, etc. On what scales do you expect these processes to occur and how will this smearing effect impact your analyses? On the other hand, the CALIPSO lidar data have very high spatial resolution, but really are only used qualitatively in this study. I would expect that there are reasonably close coincidences of CALIPSO with the trajectories on most days. Why haven't you compared the CALIPSO data with the model calculations in a more quantitative fashion? For instance, you could compare CALIPSO and modeled backscatter and aerosol depolarization ratios along the trajectories as a consistency check for the model.

Specific Comments:

P.1, L.27-29: Minor point- the use of 'conversely' here seems inappropriate. 'Conversely' suggests to me that denitrification isn't important for ozone depletion, but I would argue that it is indeed important, but there are potentially compensating processes that produce a small net effect on these short time scales. On longer time scales, denitrification is certainly important for delaying deactivation.

P.2, L.58: You state here that Antarctic PSCs are predominantly type NAT? Is this by relative frequency of occurrence or spatial extent? Is this based on one specific climatology? As has been pointed out by numerous papers, PSCs are commonly non-equilibrium mixtures of NAT particles in varying number densities and liquid binary/ternary droplets. Are your 'type NAT' PSCs actually liquid/NAT mixture PSCs.

P.2, L.100: How close to McMurdo did the trajectory pass after ten days? 300 km

doesn't seem that close, especially if you are near the vortex edge. How do you know the same air mass was sampled with the second balloon and lidar measurements?

P.3, Section 2.3: You don't mention the horizontal resolution (cross-track and along-track) of the MLS or MIPAS instruments, which can be hundreds of kilometers. I think this information is relevant to the study and should be mentioned here.

P.3, Section 2.3: The coincidence criteria for MLS and MIPAS is about +/- 200 km and for CALIPSO is about +/- 100 km. Given the spatial variability of the gas species, PSCs, etc., how do changing these criteria impact the comparisons?

P.3, L.232: CALIPSO and Aura are in the same orbit, but Aura was repositioned in early 2008 and now CALIPSO and MLS make measurements within about 30 s of one another. MLS profiles are separated by about 165 km along the orbit, while CALIPSO samples on a much finer horizontal resolution of $\sim$1 km in the lower stratosphere. See Lambert et al., Atmos. Chem. Phys., 12, 2899–2931, 2012 for more details.

P.4, Section 2.5: I'm somewhat familiar with the standard ZOMM, but not the column version. Can you describe in a little more detail how sedimentation is handled? Does it assume that the entire column of air is moving at the same velocity and in the same direction (i.e. no horizontal or vertical shear)? Are these reasonable assumptions in this case? I could imagine near the vortex edge this would not be the case. How do these assumptions potentially impact the results?

P.4, L. 303-305: Are these MLS measurements assumed to be representative of the total (gas phase + condensed phase) abundance? How is uptake on PSCs estimated? Can the coarse resolution of MLS accurately capture the scales of the processes of interest?

P.4, L. 325-326: How far did the balloon fly downwind from McMurdo during the four hour flight? How much variability was there in the lidar measurements over the four hour period? This would provide some insight into how homogeneous the PSC field was.

P.4, L.335-340: Is it likely that there were also STS droplets present in this ‘NAT’ cloud? What number concentration of STS is present?

P.4., L.358: Same comment as earlier- do you think 300 km is sufficiently close for an overpass to assume the balloon and lidar are sampling the matched air mass?

P.5, L.367-370: Can you speculate on what caused the very different ozone values in the uppermost part of the soundings? Is this a chemical or dynamical effect? Does this imply that the air in the column may be exposed to horizontal or vertical shear and therefore the ZOMM column model would not be representative?

P.5, L.376-378: Are these ozone losses observed in the past also representative of the ten-day time scale of this study?

P.5, L.400: Why are there not more MLS values coincident with CALIPSO in Fig. 3? Am I misinterpreting the figure?

P.5, L.404-422: It seems like you could find good coincidences with CALIPSO on almost every day-or at least find a representative CALIPSO orbit. Are there CALIPSO orbits available on 10-15 September, but not shown? The CALIPSO data as currently used does not add much to the paper- other than show that there was a PSC in the area.

P.5, Section 3.2: See general comment above about estimates of condensed HNO3. I don’t believe 20 ppb is reasonable.

P.5, L.460-464: How reasonable is the descent of the cloud from 17-14 km to 16.5-13.5 in 6 days? What size particles and fall speeds would this correspond to? Is this consistent with the size distribution observed with the OPC? Does CALIPSO observe a similar vertical descent of the PSC? Is there any signature of renitrification in MLS data at the lower altitudes after the PSC evaporated?

P.6, L.512-519: This is true for all of the comparisons and should be discussed much earlier (e.g. Section 2.3). Can you elaborate more on how this may affect your analyses- does it limit your conclusions?

P.8, L.719-732: How dependent are your conclusions on the time scales and spatial scales of the case you’ve analyzed? Do you think the impact of denitrification on ozone depletion remains small over the course of the spring?

Figure 3: Much too small! I had to enlarge this significantly to even see the MLS and CALIPSO measurement locations and trajectories. This needs to be much larger.

Technical

P.6, L.546: “Groo” should be “Grooß.”

P.6, L.568: “Groo” should be “Grooß.”

P.7, L.596-598: Citation is missing.

P.8, L.706: ‘as will be discussed later’ - is this really discussed ‘later’?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 32629, 2014.