acpd-2016-433 Reply to Referee Comments

Early winter Antarctic PSCs and HNO_3 observed by CALIOP and MLS

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We thank the reviewers for their careful reading of the manuscript and appreciate their suggestions for improvements. We address their comments in the following text and outline our plan for submitting a revised manuscript accordingly.

Referee Comments RC1/RC2 are in blue type.

Author Responses are in red type.

RC1 General Comments:

In this paper, Lambert et al. investigate in detail the start of the PSC season in the Antarctic stratosphere with the aim to explain the early formation of nitric acid trihydrate (NAT). For this, a decade of quasi-simultaneous observations of HNO3 (and H2O) by the MLS instrument on Aura and PSC measurements by the CALIPSO lidar are utilised. The authors argue that observed early loss of HNO3 from the gas-phase without coincident detection of PSCs by CALIPSO is due to the formation of large NAT particles of low number density. These findings are corroborated by trajectory calculations indicating temperatures some Kelvin below the NAT equilibrium temperature as a prerequisite for the occurrence of such situations. This supports early NAT formation mechanisms without the necessity for the existence of ice particles, thus backing previous observations in the Arctic wintertime stratosphere. Further, a comprehensive overview of ten years of MLS and CALIPSO early-Antarctic wintertime observations shows the relative strength of NAT versus STS formation in each year. The paper is well written and conclusive. Especially I would like to point out the effort the authors have taken in the development of new methods of data presentation to support their argumentation. Thus, I strongly support its publication in ACP. The only major points I would like the authors to consider are: (1) is the discussion of the IR limb-instruments sensitivity of any help for the flow of the arguments or does it perhaps distract the reader from the important points? (2) I miss a more in-depth discussion on measurement restrictions, like the accuracy of MLS and the lack of observations in the central part of the vortex, on the conclusions drawn.

We will address the concerns of the referee in the modified manuscript and aim to improve the discussion of the sensitivity of IR limb instruments and the inherent measurement uncertainties in our analyses.

RC1 Specific Comments:

P4L30: ‘scaled potential vorticity’ Please add a reference for sPV or a short explanation.

We will include a short explanation in the text and cite an appropriate reference for sPV.

P5L20: ‘with single-profile precisions of 4-15% Lambert et al., 2007) and 0.7 ppbv for HNO3 (Santee et al., 2007)’. Could you also give estimates on the accuracy of H2O and HNO3 from MLS in the wintertime high-latitude regions (systematic error estimation and/or comparison with independent observations)? How strong would errors in those gases affect your following argumentation?

We will address this concern by stating the estimated accuracies from MLS and providing the equivalent uncertainties in the derivation of TICE and TNAT obtained by error propagation.

P6L3: ‘Typical lower stratospheric polar values for TICE and TNAT are 188 K and 195 K, respectively.’

These values depend on pressure, H2O and HNO3. Could you indicate the ranges?

Yes, we will provide a compact tabulation of TICE and TNAT (and their uncertainties) against pressure for typical H2O and HNO3 ranges.

P8L16: 'For a mid-infrared limb sounder operating in the window-region near 12 um we use an extinction threshold, kext = 4 10 5 km 1 based on measurements by the Improved Stratosphere and Mesosphere Sounder (Lambert et al., 1996).' Also e.g. P8L22,P10L29.

Generally, I do not understand why IR limb sounders are included in the discussion while such measurements are not used at all in the scientific argumentation of the paper. Furthermore, such a threshold depends very strongly on instrumental details like e.g. spectral noise, field-of-view and radiometric calibration accuracy. I would not assume it justified to use here thresholds determined for an instrument (ISAMS) which has not been operated in parallel to CALIPSO and MLS but to skip MIPAS and HIRDLS. In addition, after the paper by Lambert et al, 1996, there have been findings regarding simulation of limb radiances and the importance of scattered mid-IR radiation (e.g. Höpfner, 2004) which do also impact the argumentation on sensitivity (by increasing the sensitivity for particles larger than 1 um). In conclusion, I would suggest to either go into more detail regarding the IR limb-sounding thresholds (instrumental parameters, refractive indices used for STS and NAT, forward model including scattering: : :), or, perhaps better, skip this discussion and concentrate on LIDAR and MLS.

We would prefer to add further supporting material on the capabilities of IR limb sounders for aerosol/PSC detection. UARS ISAMS/CLAES/HALOE were of course operated in a period of enhanced stratospheric aerosol loading from Mt Pinatubo. We can also bring into the discussion the contemporary measurements from MIPAS and HIRDLS to provide a more inclusive analysis of the performance of the IR limb sounders. In particular, in a comparison of CALIOP and MIPAS PSC measurements, Hopfner et al (2009) (*Comparison between CALIPSO and MIPAS observations of polar stratospheric clouds, J. Geophys. Res., 114, D00H05, doi:10.1029/2009JD012114*) found a discrepancy in the number of Antarctic PSC detections during May.

In Lambert et al (2012) *(A-train CALIOP and MLS observations of early winter Antarctic polar stratospheric clouds and nitric acid in 2008, Atmos. Chem. Phys., 12, 2899-2931, doi:10.5194/acp-12-2899-2012, 2012)* we commented on the findings by Höpfner et al as follows . . .

> *Comparisons between CALIOP and MIPAS matching pair observations by Höpfner et al. (2009) in 2006-2007 found that overall both instruments detected Antarctic PSCs in common in 85% of the matches during June-August, but only 60% in May. In particular, there were considerably more MIPAS-only PSC detections (i.e without corresponding matching detections by CALIOP) in May (25%), compared to June (8%) and July-October (< 3%). Höpfner et al. (2009) attributed these more frequent detections to the MIPAS limb-viewing geometry, which is oriented towards the pole, and results in sensitivity to PSCs lying poleward of the tangent points, but beyond the latitude limit of the CALIOP nadir view. Since PSC formation largely occurs in a region close to the South Pole in May, the MIPAS viewing geometry has a much larger effect on the PSC detection frequency at this time compared to later times when PSCs occur over a more widespread region. Note that the MLS line of sight is in the forward direction along the orbit track and is not oriented towards the pole, therefore the low HNO3 measurements are not biased by the viewing ge-*

> *ometry.*

Our analysis of Antarctic early-winter PSCs now extends to a decade of measurements and provides conclusive evidence that another factor, other than viewing geometry of cloud inhomogeneity, is also at play in the lower number of Antarctic PSC CALIOP detections in May compared to MIPAS – the common occurrence in some early winters of large particle NAT clouds which are not detected by CALIOP.

Since we submitted our manuscript a new paper on the MIPAS PSC classification scheme has been published by Spang et al (2016) (*A multi-wavelength classification method for polar stratospheric cloud types using infrared limb spectra, Atmos. Meas. Tech., 9, 3619-3639, doi:10.5194/amt-9-3619-2016, 2016.*). This paper presents an intercomparison of CALIOP vs MIPAS PSC detections and statistics on the frequency of type classifications that are relevant here and we plan to discuss these findings in our modified text. Particularly, we note that only the climatological averages of PSC count statistics over the entire May-October period are presented in Spang et al and not shown monthly as in Höpfner et al. (2009).

P9L2: 'The morphology of NAT particles is still an open question, as is the compactness of the particles (Molleker et al., 2014; Woiwode et al., 2014).' One could also mention here a recent publication by Woiwode et al., 2016.

We will add a reference to this paper which was published in ACP after we submitted our manuscript.

P15L13: 'However, further averaging of CALIOP backscatter (as discussed in Section 3) on 27 May (not shown) does indicate a considerably larger area of MIX1 class, and so it appears that we are dealing with the limit of the L2PSCMask detection range.' Where does this extended area lie? Below (indicating sedimentation) or in the TTE region? Maybe a figure could be added as supplemental material

The extended area of MIX1 lies mainly to the left of the STS cloud. We agree with the suggestion of adding a new figure as the effect is even more profound than the Figure 3 illustration.

P15L20 and Fig. 9: 'can lead to a complete removal of the available ambient HNO3 from the gas phase.'

Could you comment on the large amount of negative HNO3 values. Are those compatible with the MLS precision or does it hint to some systematic error?

We considered the underlying measurement uncertainties from MLS and the GEOS temperatures in Lambert et al 2012 . . .

> *4.3.2 Measurement uncertainties*
> *Uncertainties in the temperature analyses and nitric acid measurements contribute to the scatter of the data in Fig. 5. We note that in situ measurements of the aerosol volume density variation with temperature have shown excellent agreement with the calculated STS equilibrium curve (e.g., Drdla et al., 2003) and hence may indicate for the results here a low bias of about 1K in the GEOS-5 temperatures. The mean*

> *value of the HNO3 data for the ICE classification is 0.3 ppbv, which could imply an actual total uptake of available HNO3 in the presence of ice PSCs since we are unable to rule out such a small positive bias in the MLS HNO3 measurements. The standard deviation is 0.5 ppbv, which compares well with the estimated MLS single measurement precision of 0.7 ppbv.*

We will improve the discussion of the measurement uncertainties and add a reference to these previous findings.

P17, chapter 6: I would like to see some discussion on the centeredness of the polar vortex around the S-pole between the different years and whether this correlates somehow with the presented data especially related also to the central part, which is missed by the observations.

We will investigate the extent to which the polar vortex wanders around the South Pole and indicate how this interacts with the data gap poleward of 8 degrees in the revised manuscript.

P40, Fig. 10: Could you show here also T-Tice (e.g. in the appendix)? Does this look significantly different from TTE?

For the 32 hPa pressure level, TTE and T-TICE are shown together in Figure 13 for all years investigated including 2009. Fig 8b shows detailed cross-sections during May 2009 with clear differences between the structure of the local temperatures (T-Tice) (color shading, with T=TNAT and T=Tice + 2 K contours) and TTE.

Technical corrections:

We will make the corrections noted in RC1 in the revised manuscript.

RC2 General Comments:
This is a complicated and comprehensive over view of what may be learned by combining co-located remote measurements of gas phase HNO3 from the Aura microwave limb sounder (MLS) and the CALIOP lidar measurements of particle backscatter and depolarization. The authors combine these measurements with back trajectory calculations to address questions related to the nucleation of nitric acid trihydrate (NAT) within polar stratospheric clouds. The primary conclusion that there is significant NAT formation at temperatures well above Tice for NAT with low number concentrations and large particle sizes implies that particle observations confirming this conclusion are not possible due to the sensitivities of the lidar measurements. Thus a significant fraction of the paper is devoted to microphysical calculations of the sensitivities of the various instruments to particles of varying sizes, number concentrations, and shapes. This is necessary to ultimately rely solely on the MLS measurements of HNO3 gas phase loss as evidence of PSC formation when concomitant particle observations provide no measurable PSCs. Thus the primary conclusion on NAT nucleation requires only MLS gas phase hno3 loss and an absence of PSC detection by the CALIOP lidar. The authors present a lot of information in fairly compact forms and it is difficult to suggest any effective ways to shorten or compress the figures. The color coding can be at times difficult to fully distinguish the various categories of particle calculations and I wonder if all the aspect ratios presented are necessary. I should think the aspect ratios bounding the range are sufficient. It is not clear why the sensitivities to IR measurements at 12 um are presented. No IR measurements are used in the analysis and none are currently available for PSC measurements to my knowledge. Is this just done for completeness? In any case the slant indicating the IR measurements are somehow more sensitive to PSCs based on the graphs shown seems a bit arbitrary. The IR emission measurements will be more sensitive to larger particles since they are sensitive to volume whereas the visible scattering measurements are sensitive to aerosol cross section so more sensitive to smaller particles.

We will address the concerns of the referee in the modified manuscript. The different aspect ratios are provided to indicate that they do not change monotonically. The discussion of the IR measurements will be expanded and better justified, as also suggested by the first reviewer.

The paper should be published with minor corrections. I provide some specific comments for consideration below.

5.6-13: This is too much detail that will make sense to the very few who know what PSC compositions of 2 and 3 are. I would recommend a short description of what the distinction between mix1 and mix2 is and why it is important, then just explain that the separation failed to include in mix1 those observations with a scattering ratio less than 1.25. Later 1.25 is used as a threshold to identify PSC presence so overall this is a bit confusing.

We will incorporate the suggested simplified explanation into the text. However, the MIX1/MIX2 mis-classification still remains as an undocumented error in the v1 L2PSCMask operational dataset.
`http://www-calipso.larc.nasa.gov/resources/calipso_users_guide/data_summaries/psc/index.php`.
Accordingly, we feel that it is necessary to document in detail the precise algorithm we actually used to correct the supplied PSC classification.

We will reorganize this section to make a better distinction between our specific usage of the v3 Level-1b standard product and the v1 Level-2 L2PSCMask.

6.2: 'The HNO3 and H2O values (for estimating TNAT and TICE) are assumed to be the same at all back-trajectory times.' This does not make sense. The same as what? Are they assumed to be constant from the start point of the back trajectory, so not updated along the trajectory, or ???

Yes, HNO3 and H2O are assumed to be constant from the start point of the back trajectory and we will clarify this in the revised manuscript.

8.8: Do the authors believe there is really uncondensed h2so4 available for uptake? If so what are they using for the ambient h2so4 gas phase mixing ratio?

An estimate of the total H2SO4 mixing ratio is required for the supercooled ternary solution thermodynamical calculations in the Carslaw et al formulation. It is set at 0.1 ppbv, which is an appropriate level for the lower stratosphere in volcanically unperturbed conditions. There is practically no H2SO4 vapor at the very low temperatures associated with PSC formation. However, binary aerosols (SBS) do evaporate at higher temperatures (see Fig 4, Carslaw et al 1997) and H2SO4 vapor is released.

8.15: Rt=1.25 as a threshold? This is the same value used earlier in the revised classification scheme and now here is used as a threshold to identify PSCs. Seems a bit confusing. In addition Fig. 4 c) uses 1.25 as the threshold for STS detection, so clearly NAT PSCs could appear below this level. Please clarify.

Again, we will reorganize this section to make a better distinction between our specific usage of the v3 Level-1b standard product and the v1 Level-2 L2PSCMask. Also we will indicate the sampling volumes of the respective instruments.

8.29-31 and Fig. 4c: This statement and the figure don't show that the IR is more sensitive than the visible to STS content. It just shows they are different. The ordinates in Fig 4c are somewhat arbitrarily chosen and the assumed thresholds are set on somewhat subjective criteria that are not fully justified and are different. Again for this paper what is the point of showing the IR results?

Only three spaceborne lidar missions have ever been flown (GLAS, CALIOP, and CATS) compared to many IR sounders over the past few decades. The purpose of including results from IR sounders is to provide context for the lidar measurements. We show that large NAT particles at low number densities are expected to be detected by IR limb sounders. There are conditions under which large size NAT PSCs are not detected with the CALIOP L2PSCMask, but can be inferred by the uptake of HNO3. Therefore it appears logical to provide some simulations to understand why this is the case and to compare against IR sounder capabilities. However, we agree that for STS, given the assumed thresholds that are based on practical empirical considerations, the IR measurement is only marginally more sensitive than the visible lidar, because a smaller HNO3 content within the STS is detectable. Now, one may argue that if the lidar signal had been averaged over a larger volume, then it would have been identified as the more sensitive technique. However, the lidar is limited in the across track direction to around 90 m and nothing can be done about that. We have however investigated coarser averaging of the lidar data in the along-track and vertical directions in this paper. In the case of MLS, the across-track averaging (i.e. the 240 GHz antenna beam width at the tangent point) is around 8 km, the vertical field of view for HNO3 is a few km and the along-track sampling is over several hundred km. The sampling volumes of IR instruments and MLS are therefore three or more orders of magnitude larger than the typical CALIOP sampling volumes. We will discuss these sampling issues more thoroughly in the revised manuscript.

9.18-21: Is this realistic? Would the large NAT particles not continue to take up hno3, given enough time, until it was all consumed, so additional uptake of hno3 is not dependent on STS?

This is a crude, but not unrealistic, snapshot of a possible STS/NAT mixture at a particular time. The Wegener-Bergeron-Findeisen process will indeed cause sequestration of HNO3 by NAT in a mixed phase STS/NAT cloud at the expense of the HNO3 in the liquid STS (*e.g. Voigt et al (2005), Nitric Acid Trihydrate (NAT) formation at low NAT supersaturation in Polar Stratospheric Clouds (PSCs), Atmos. Chem. Phys., 5, 1371-1380, doi:10.5194/acp-5-1371-2005, 2005.*). However, if the STS forms quickly by rapid cooling then the uptake of ambient HNO3 can be predominantly into STS rather than into NAT. Growth of NAT is then retarded at these low temperatures of a few K above the frost point, see Fig 4 of Voigt et al (2005). We will describe these processes more thoroughly in the revised manuscript.

9.30-31: Same question as above. Why does the uptake of hno3 depend on the number density of particles? Is this some sort of kinetic limit or resident time limit, i.e. particles growing too large to stay in the air space? I am not aware there is a theoretical limit to the size a NAT particle can attain given existence at $T < Tnat$ and hno3 and h2o available.

The growth of NAT is kinetically limited, see Fig 4 of Voigt et al (2005). A high number density of NAT nuclei would ultimately lead to a NAT distribution with smaller particle sizes than a low number density since the available HNO3 is spread over a large number of particles. (*Jensen et al (2002), Impact of polar stratospheric cloud particle composition, number density, and lifetime on denitrification, J. Geophys. Res., 107(D20), 8284, doi:10.1029/2001JD000440, 2002.*). Once nucleated, a NAT particle will continue to grow, providing there is sufficient HNO3 and H2O available and $T < TNAT$, such that the HNO3 vapor pressure over NAT is supersaturated, until it attains its equilibrium size (reaching a radius of tens of microns). Gravitational sedimentation may cause the NAT particles to descend into a region of lower HNO3 and/or rising temperature causing evaporation rather than growth.

We will describe these processes more thoroughly in the revised manuscript.

10.9-10: I suppose this should be no surprise since IR emission will be sensitive to volume, R3 whereas backscatter is sensitive to cross section, R2. Thus large particles cause larger changes in volume.

This is correct. Scattering is dependent on the size parameter (x = 2 * pi* radius/wavelength).

10.17: How is effective radius, Reff, defined? Is this 3V/S so the ratio of the third and second moments?

Yes.

14.25: I do not see a blue line, indicating Tice+2K, on any of the panels for case 3.

The area enclosed by this contour is hard to see. We will indicate specifically the location in the text.

15.28: I assume the authors mean 340 K (mid-June).

Yes, this should be 340 K.

16.10: Where is the gray shading? I do not see any. It only appears in later figures so save the explanation for then.

The gray shading appears in the daylight part of the CALIOP measurements in rows 8e and 8f. We will add to the Fig 8 caption “Gray shading indicates no observations”.

16.14: It takes quite a few days for significant TTE to be observed at 21 hPa, nearly half the period shown, so the statement here comparing 21 and 46 hPa for the appearance of significant TTE is confusing.

We will reword this statement on the first appearence of TTE at pressures above and below 32 hPa.

Fig 13a: Where are the diamonds in the TTE plot?

These will be rendered in white in the revised plot to improve visibility.