Response to Referee #1's Comments

We would like to thank Referee #1 for his/her time, constructive and helpful comments and suggestions.

Major comments

1) Page 22160, line 26 the authors mention that "the "STS+NAT" and "CALIPSO constrained" runs were closer to the measurements than the "STS"run." According to the legend in figure 8, "STS+NAT" is in black, "CALIPSO constrained" in blue and "STS" in grey. Thus the "STS+NAT" and "STS" runs are closer to the measurements than the "CALIPSO constrained" run. This impacts the conclusion given between page 22160 line 29 and page 22161 line 1. The authors cannot claim that the amount of chlorine activation on PSCs is dependent on PSC classification. Same remark for page 22162 line 24 and in the abstract page 22142 line 20. However, this remark are not such as to call into question the main results of the paper but should be rectified.

You are right. We agree that we cannot claim that the amount of chlorine activation on PSCs is dependent on PSC classification. Also, there is inconsistency between PSC number densities used for "CALIOP constrained" run and other ("STS+NAT" and "STS") runs, as is pointed out in the following comment 2). This inconsistency comes from different PSC models used for these runs. We discussed on this issue among co-authors, and concluded that it is no use to show these three model run results in the paper, because there is no fundamental differences in the model results to discuss. Therefore, we decided to show only "STS+NAT" model run results throughout the paper.

2) For "STS+NAT" run, the authors use a NAT particle number density of 0.1cm-3 while for the "CALIOP constrained" run, they use 10-3 cm-3. In a same manner, they use an ice

particle number density of 0.01cm-3 while for the "CALIOP constrained" run, they use 1 cm-3. In order to better compare the results of the two runs, why do the authors not use the same particle number densities?

As is stated in the above reply for your comment 1), this difference comes from the different origin of the PSC models. As is stated above, we decided to show only "STS+NAT" model run results throughout the paper.

3) The first part of the paper discusses the link between temperature evolution and CALIOP PSC composition observation. However, there is no discussion/explanation of why temperatures are sometimes below the PSC thresholds and no PSC are observed by CALIOP. This is the case in figure 4 (day 4), figure 5a (day 2), figure 5b (day 2), figure 11 (day 2), and figure 13 (day 4). This also concerns the second part of the manuscript for cases #02 (day 2) and #09 (day 4 morning) where PSC are simulated by the ATLAS model but not observed by CALIOP. Some comments should be included in the manuscript to explain these differences.

There are several possible reasons for this: A) We have to interpolate the CALIOP PSC measurements to our trajectory locations, which introduces uncertainty, since we don't really know what type of PSC is on the location of the trajectory. B) Uncertainties in the CALIOP measurements and classification. C) Uncertainties in ECMWF temperature. D) Another possible reason is that this could be real: PSC formation is a complicated process that depends e.g. on temperature history. A) is actually discussed in detail in the paper (page 22146, 4-15). B) is discussed in other papers (Pitts et al., 2007, 2009, 2011). C) is also discussed to some extent in the text. The contents of D) is out of focus of this paper.

Minor comments

1) Page 22146, lines 4-9. Could the authors specify the maximum time difference between CALIOP measurements and the trajectory points? For the distance, it is less than 100-200 km?

The maximum time difference is 24 hours. We have added the description 'closest to each trajectory point "on the same day"' on page 22146, line 5. You are correct that the distance is typically around 100-200 km. We hope that is implicitly clear from the statement on page 22146, line 14-15.

2) Figure 2. Could the authors better explain how they get the CALIOP field? As CALIOP data are only available where circles are, how the PSC composition between these circles is determined? The method detailed page 22147 to get the PSC field is not clear.

We have added the description "Global PSC field was created by selecting the closest CALIOP PSC measurement on the same day." at the end of page 22147, line 18.

3) In this study, the authors use the MLS version 3.3. The MLS version 4.2. is now available but for HCl and O3, it seems that there are very little or no change compared to V3.3/V3.4 according to the "version 4.2x Level 2 data quality and description document" (JPL D-33509 Rev. A). Page 22146, line 22, the authors can mention that they also use H2O data as explained page 22153 line 6.

At the time when the calculations were made, no version 4.2 data was available. We added H2O as a species on page 22146, line 22.

4) Page 22147 line 14, the authors should change "below TNAT" to "above TNAT".

"below" is correct here. It refers to "period" and not to "sudden stratospheric warming".

5) Page 22150, lines 3-5, could the authors give a reference for this value of supersaturation needed?

We have added references.

6) Page 22150, line 26, could the authors indicate the value of the assumed supersaturation for HNO3 over NAT? Is it 10 as mentioned before?

This is the general model description, and the value for the supersaturation is not fixed in the model. Hence, the value is only given in section 4.2, where the actual model setup for the specific runs is described.

7) Page 22155, line 23, to help the reader, the authors should add the reactions :

ClONO2+HCl–>HNO3+Cl2

ClNO2+H2O–>HNO3+HOCl

HOCl+H2O–>Cl2+H2O

When the authors mention from page 22143 line 28 to page 22144 line 3 the reaction partner, I suppose that they refer to these reactions.

Thank you for the suggestion. We added these reactions on page 22143, and showed the number of reaction (1) on page 22155.

8) Page 22156, lines 3-5, could the authors indicate why the ATLAS model needs larger spatial and time scales to reproduce HNO3 measurements?

Since the discussion on O3 and HNO3 is not essential part of this paper, we deleted all the discussion on O3 and HNO3, and related panels from the paper completely.

9) For figures 8 to 14, it is necessary to use a 400 % zoom in order to read the figures and see the differences between black, grey and blue curves. The authors could probably only focus on the part between days -1 and days 5. The figures are very well described in the legend. However, explanation about the short backward trajectories observed on figures (d) to (i) is missing. I assume that these are the short back trajectories done to find the last model output of the global model for chemical initialization. Likewise, on figures 8 to 14 (h), there are dotted lines not explained in the legend. I expect it represents the HNO3 total (gas phase and condensed).

We need the time axis from -5 to +5 days, since the trajectory is initialized by the MLS measurement of the last 5 days which is described in section 4.3, and these are shown in the plot. The all O3 and HNO3 panels are deleted from the paper (see reply to your comment 8).

Response to Referee #2's Comments

We would like to thank Referee #2 for his/her time, constructive and helpful comments and suggestions.

<General comments:>

The authors examine in their study different topics with the help of several trajectories calculated with ATLAS. In my opinion this method is innovative and appropriate for the performed study.

Thank you very much.

From about 30 calculated trajectories, they choose eleven for their study. Unfortunately it is not clear, what kind of criteria they use to choose these eleven trajectories. For example number 3 and 4 are very similar. That issue should be cleared by the authors.

The way of selecting the trajectories is described in Section 3.2 in detail. The selected eleven cases are chosen to cover several different PSC composition classifications and different temperature histories. We agree that case #03 and #04 are rather similar. Therefore, we deleted case #03 from the draft.

In the result section 5.1 (with the help of Figs. 5 to 7) Nakajima et al. discuss the dependence of PSC classification on their temperature history with the help of CALIOP measurements on different chosen trajectories. The authors conclude that the kind of formation of the PSC types

depends on the temperature history. In cases of rapid temperature decrease first STS is formed, followed by NAT/STS clouds. When temperatures dropped below the frost point, ice clouds formed, and then transformed into NAT/STS mixture when temperature increase above the frost point. This part of the manuscript I find very interesting and the results are in my eyes relevant for publication.

Thank you very much.

In section 5.2 (with the help of the Figs. 8 to 11 and 13) the authors compare the results of the ATLAS model with MLS and CALIOP measurements. They performed for this comparison three different model runs: "STS+NAT" (I think this is the standard run), "STS" and "CALIPSO constrained".

The comparison of HCl, and ClO between ATLAS and MLS is in general very good, although ATLAS in many cases doesn0t match correctly the PSCs from CALIOP and the authors can show that chlorine activation is limited by the amount of available ClNO3.

But the comparison of HNO3 fits not very well and the O3 comparison is difficult because there are only small variations in ozone on the selected trajectories. The authors write that the ALTAS model cannot reproduce the denitrification for a single trajectory (page 22156, line 3-7). In this case I would suggest to skip the HNO3 and also the O3 comparisons.

We agree that denitrification is difficult to simulate for a single trajectory. Since HNO3 is not the essential part of this paper, we deleted all the discussion and panels on HNO3 from the draft. Also, simulated and modeled O3 depletion on the trajectory is small, because no enough sunlight is available in this period of year. Therefore, we also deleted the discussion and panels on O3.

In general I would also recommend to examine one or two less trajectories studies, because there are in my opinion too much similar figures to consider. Maybe it would also be a solution to add a supplement with more trajectory cases.

We disagree to reviewer's comment on this point. Each trajectory case shown in the draft represents different temperature history and different PSC classification history on the course of trajectory. Therefore, we kept all figures in the current draft.

Moreover I don't see really the relevance of the both sensitivity runs ("STS" and "CALIPSO constrained"). In my opinion there is no real improvement shown through the results of these sensitivity runs. Especially if the setup regarding the number density of NAT and ice particles in the "STS+NAT" run and "STS" run is different as in the "CALIPSO constrained" run (Sect. 4.2) it should be considered to skip all results of the sensitivity runs from the figures and remove the corresponding discussion in the publication.

We agree to the reviewer's comment on this point. There is not enough differences between the three sensitivity runs. Moreover, the number densities used for these runs are different, because different PSC scenarios were used for these runs. Therefore, we used only "STS+NAT" run results, and deleted results and sensitivity runs part (Section 4.2) from the draft.

In Section 5.3. (with the help of Figs. 12 and 14) Nakajima et al. confirm that the formation of PSCs are very temperature dependent with the help of two another sensitivity runs (+1K and -1K temperature runs). The authors claims that the run with decreased temperatures fits better with the observations. But in my opinion this is at the most valid for HCl. With focus to the surface area density, ClO or HNO3 I don't see really an improvement. The conclusion that the formation of NAT is temperature dependent is in my opinion not really new. I would suggest also to remove this subsection or at least to choose different trajectories with better results.

The comparison with HNO3 is difficult by ATLAS model as is explained above, and we deleted HNO3 panels from the draft. The purpose of showing Figs. 12 and 14 is to represent

that chlorine activation is very sensitive to temperature. Therefore, we keep these figures and discussion in the draft.

<Specific comments:>

Page 22142, 16-17: In my opinion the ATLAS model results only agree well with the observations in the case of HCl and ClO. Please add this here.

Since we deleted discussion on HNO3 from the draft, we think that the current description is OK.

22143, 4: If you mention that STS is H2O-H2SO4-HNO3, perhaps you should also mention that NAT is HNO3(H2O)3

We added the suggested description there.

22143, 21: Voigt et al., 2005 and Hoyle et al., 2013 only assume heterogeneous nucleation of NAT on meteoritic dust. Biermann et al., 1996 showed in laboratory experiments that heterogeneous nucleation rates on micrometeorites are too low to enhance freezing of polar stratospheric clouds above the frost point.

We added description on Biermann et al. (1996) there as you suggested.

22143, 24: "(and hence strongly on temperature)".

239 Changed as suggested.

240

241 *22144, 7-8: I don't know if you really can answer the second question with your study. It's*
242 *really difficult to evaluate the sensitivity of chlorine activation or ozone depletion on different*
243 *PSC types with your study. Moreover there is in my opinion no chemical ozone depletion*
244 *shown on your trajectories neither by the simulation results nor in the observations.*

245

246 You are right that it is difficult to study on the difference of chemical ozone depletion to
247 different PSC composition by our current study. We deleted description for ozone from the
248 text.

249

250 *22146, 1-2: What is the reason that you use only three instead of at least four categories (STS,*
251 *Mix1, Mix2 and ice)?*

252

253 Mix1 and Mix2 are the categories both of which include so-called "NAT" PSC. Therefore,
254 we used conventional three PSC categories, STS, NAT, and ice.

255

256 *22147, 6-11: In my opinion you don't have to describe the legend to the figures in the caption*
257 *and in the text.*

258

259 We deleted some sentences from the text.

260

261 *22150, 3: What is the meaning of supersaturation of 10? 10 percent?*

262

263 We have changed "about" to "of a factor of".

264

265 *22150, 7-9: What criteria do you use to choose these eleven trajectories?*

The way of choosing the eleven trajectories is to cover several different PSC composition classifications and different temperature histories. We added this description in Section 3.2.

22150, 22: Please cite Dee et al. 2011 for the ERA-Interim reanalysis.

Cited as suggested.

22150, 23: . . .are allowed to form in parallel. . . (?)

Changed as suggested.

22151, 16: . . . the maximum particle number density?

The number density is constant. See Wohltmann et al., 2010.

22151, 18: . . . of 10 %?

See reply to comment to page 22150, 3.

22152, 12: Please explain why do you use here a much smaller NAT number density as in the "STS" and "STS+NAT" runs?

Since the "CALIOP constrained" run used different PSC scenario compared with other ("STS" and "STS+NAT") runs, their assumed PSC number densities were different. As is pointed out

by your General comments, we found that there is not enough differences between the three sensitivity runs, so we decided to show only "STS+NAT" run results in the draft.

22152, 15: Here the same: why do you use here 1 cm-3 instead of 0.01 cm-3?

Please see the reply above.

22154, 3: In table 1 are eleven selected trajectories not nine

We discussed nine (now eight, deleted one case in new Fig. 5 following a reviewer's comment that old case #03 and #04 are very similar) cases from table 1 for PSC evolution by temperature history. Other three cases (#02, #03, and #09) are used for temperature sensitivity study (Figs 11/12, and Figs 13/14).

22154, 9: "When temperatures warmed above T_{NAT} in trajectory case #1. . ."

Changed as suggested.

22154, 23: Please add a citation for this "old theory" of NAT PSC formation

Added Koop et al. (1995) as a citation for this "old theory".

22154, 25: In my opinion the temperatures are never below T_{ice}.

We changed "below T_ice" to "near T_ice".

22154, 25-28: The first sentence is maybe okay, but I don't know if this is really a proof for the accuracy of the ERA Interim temperatures. I would say maybe a hint. But you have to delete in any case the second sentence. It is presumptuous to claim that the ERA Interim temperatures have an uncertainty of 1 K, because your model fits better with 1 K lower temperatures.

Your comment is right. We have deleted the second sentence.

22156, 3-7: If it not possible to simulate the denitrification with ATLAS on your trajectories, why do you use ATLAS then for this study? Or why do you show then comparisons of HNO3 and also of O3 between the model and the measurement? That make no sense in my opinion.

We agree. We deleted panels and discussion related to O3 and HNO3.

22156, 22-23: Cl2 can't be photolyzed to ClO_x because Cl2 is part of ClO_x.

Cl2 is photolyzed to Cl, and then form ClO, which is a part of ClOx. We rephrased in the text. We mistook the legend of ClOx in panels (f) (new panels (e)) of Figures 8 to 14. We changed the species shown in panels in Figures 8 to 14.

22156, 27: I don't see a chemical ozone depletion neither in ATLAS nor in the measurement. ClO is the product of O3+Cl -> ClO, Cl is the reason for O3 depletion, not ClO.

You are right. There is very small O3 depletion modelled by ATLAS at around day 2.8 and 3.5, when small solar illumination was available, which was shown by orange dots on the top of panel (i) in Figure 9. However, O3 depletion is not the main issue of the focus of this paper, we deleted description related to O3 from the draft.

22157, 11: Cl2 is photolyzed to Cl, not to ClO.

See reply to comment 22156, 22-23. The text was rephrased.

22157, 12: I would say "slightly" is the wrong word for this depletion.

All the discussion on HNO3 is removed from the manuscript.

22157, 13-15: Again I don't see really an ozone depletion.

We deleted description related to O3 from the draft.

22157, 28-22158, 2: Why do you have such a decrease in HCl and ClNO3 in the STS run (and also in the STS-NAT run), although you simulate only a very small PSC surface area?

Surface area density does not directly translate into reaction rates. The reaction rate is also dependent on the amount of ClONO2 available and temperature. E.g., in Figures 8-10, the model just runs out of ClONO2. In this case, it does not matter that the surface area densities are much larger.

22158, 12: Is the result of the -1 K model run really better than the standard model run? In the first simulation you have in average smaller values as measured, in the second simulation you have in average higher values as measured. In my opinion both runs fit well with MLS regarding HCl. But in both runs the simulated PSCs don't match the observations and also the denitrification is not really better in the -1 K run.

Since there is not enough difference between three PSC model runs, we only show "STS+NAT" run results in the draft. We believe that temperature difference of 1 K is important for the simulation result.

22158, 13-15: That is surely a correct suggestion, but not really a new result, or?

We modified the text to refer earlier result by Carslaw et al. (1994).

22158, 24-26: You have also to delete this sentence. There is really no proof in your study for any uncertainties in ECMWF temperatures.

The sentence was deleted as suggested.

22159, 1: Surely the HCl results are better in this case with the -1 K model run, but quite well?

We want to keep as it is.

22160, 13-15: This is also my opinion. What is the reason that you show the results of all these scenario runs in this publication?

We modified to show only "STS+NAT" result in the draft.

22161, 20-23: If you write as on page 22159, 18-19, that your study "suggest the possibility of heterogeneous nucleation of NAT on solid particles" I can live with it, but here you mention again the meteoritic dust, although you write on page 22159, line 16-17 that this case is unlikely (Biermann et al., 2006).

We added the description on Biermann et al. (1996) here as well as on page 22159.

22162, 11: Please write here ClO instead ClO_x.

Changed as suggested.

22162, 24-27: It is not true that the temperature explain most discrepancies between model and observation. Please correct this sentence. Also in the -1 K run you don't match PSC periods from CALIOP or the HNO3 MLS measurements.

We rephrased here to more focus on modeled and measured HCl discrepancies. The PSC field is created by taking the closest CALIOP measurement, and sometimes not represent the fine structure of actual PSC field. (Please see our reply to other referee (#1) major comment 3.)

< FIGUES >:

Fig.1: last sentence: ".. and the Type II (ice) frost point temperature .."

Changed as suggested.

Fig.3: Can you please also plot the colour bar which indicates the different PSC types in the panels b and c. This is in my opinion important because the colour code is different to panel a (otherwise it is confusing). If it possible it would also be great to write the longitudes and

latitudes to the horizontal axis of panel b and c (in the same way as in panel a). In panel c you have two blue lines, maybe you can choose light blue in one case instead of blue.

Color bar which indicates the different PSC types were added in panels (b). The longitudes and latitudes was not added to panels (b) and (c), because it is not a very useful information for the reader. The color of PSC saturation temperature was modified as suggested.

Fig.4. to 14: Same as in Fig. 3: Please add a colour bar with the PSC types and the latitudes and longitudes of the trajectories.

Changed as suggested. The latitudes and longitudes of the trajectories were not added.

Fig.5: a) Can you please add in the caption at least the information about time and altitude and/or pressure for the trajectories cases? b) Why is the sequence #1, #4,#3 and not #1,#3,#4 c) Why do you show #3 and #4 both, this trajectories have more or less the same conditions due to the very similar starting point? d) Again information about the latitudes and longitudes of the trajectories and a colour bar would be great.

The time and altitude information was added to the caption of Fig. 5. The sequence was re-ordered. The case #03 was removed. The color bar was added. Latitudes and longitudes of the trajectories were not added.

Figs.6. and 7: Same as in Fig.5: More information would be great and the sequence is strange.

Cases were re-ordered.

Fig.8: a) Temperature of trajectory case #3 is only displayed in Fig.5 not in Figs.5-7. b) It's difficult to read the titles and the units in the panels. c) In general the panels are very small (maybe this is better in the final paper?). For example the line of the grey curve of the STS run is extremely difficult to see. d) In Fig. 8h I see also a dashed blue line. What is the meaning of this line or is this a mistake?

Since we deleted old panels (c) Rates, (h) HNO3, and (i) O3, the new figures 8-14 consists of six panels. We hope this will improve the readability of each line. The HNO3 panel (h) was deleted.

Fig.9: There is again this dashed blue line in panel h.

The old HNO3 panel (h) was deleted.

Fig.12: a) There are again dashed blue lines in panel h. b) The comparison of measurements and model is in the -1 K run not very good. The surface area density and the HNO3 don't match the observations. Why do you select this trajectory? Is this really the best comparison you have (you write you analysed more than 30 trajectories).

The old HNO3 panel (h) was deleted.

Version 5.2a~~4.7f~~

31~~15~~ January~~July~~ 2016~~5~~ (Sun~~Wed~~)

Polar Stratospheric Cloud evolution and chlorine activation measured by CALIPSO and MLS, and modelled by ATLAS

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Abstract

We examined observations of polar stratospheric clouds (PSCs) by CALIPSO and of HCl~~,~~ and ClO ~~and HNO_3~~ by MLS along air mass trajectories to investigate the dependence of the inferred PSC composition on the temperature history of the air parcels, and the dependence of the level of chlorine activation on PSC composition. Several case studies based on individual trajectories from the Arctic winter 2009/2010 were conducted, with the trajectories chosen such that the first processing of the air mass by PSCs in this winter occurred on the trajectory. Transitions of PSC composition classes were observed to be highly dependent on the temperature history. In cases of a gradual temperature decrease, nitric acid trihydrate (NAT) and super-cooled ternary solution (STS) mixture clouds were observed. In cases of rapid temperature decrease, STS clouds were first observed, followed by NAT/STS mixture clouds. When temperatures dropped below the frost point, ice clouds formed, and then transformed into NAT/STS mixture clouds when temperature increased above the frost point. The threshold temperature for rapid chlorine activation on PSCs is approximately 4 K below the NAT existence temperature, T_{NAT}. Furthermore, simulations of the ATLAS chemistry and transport box model along the trajectories were used to corroborate the measurements and show good agreement with the observations. Rapid chlorine activation was observed when an airmass encountered PSCs. ~~The observed and modelled dependence of the rate of chlorine activation on the PSC composition class was small.~~ Usually, chlorine activation was limited by the amount of available $ClONO_2$. Where $ClONO_2$ was not the limiting factor, a large dependence on temperature was evident.

1. Introduction

Soon after the discovery of the Antarctic "ozone hole" (Farman et al., 1985), it was established that heterogeneous reactions on polar stratospheric clouds (PSCs) play an important role in ozone destruction (Solomon et al., 1986; Portmann et al., 1996; Solomon et al., 2015). They are the first step in the conversion of chlorine reservoir species ($ClONO_2$ and HCl) to highly reactive radical species (Cl, ClO) which drive catalytic cycles that destroy ozone (e.g., Molina and Molina, 1987).

PSC particles may be solid, consisting of ice (cf. the historical overview by Peter and Grooß, 2012) or nitric acid trihydrate (NAT: HNO_3-$3H_2O$) (Crutzen and Arnold, 1986; Voigt et al., 2000). Alternatively, they may also be liquid H_2O-H_2SO_4-HNO_3 droplets (super-cooled ternary solution = STS) (Carslaw et al., 1994). Liquid and solid particles can coexist over a wide range of conditions (Koop et al., 1997; Pitts et al., 2009).

The mechanisms by which NAT particles are formed have provoked some controversy (for a review, see Peter and Grooß, 2012). Laboratory measurements have shown that homogeneous nucleation of NAT in H_2O-H_2SO_4-HNO_3 solutions is kinetically limited, and thus cannot be expected immediately after the existence temperature of NAT ($T_{NAT} \approx 195$ K in the lower stratosphere) is reached (Koop et al., 1995). Another proposed NAT formation mechanism is heterogeneous nucleation on ice particles (Koop et al., 1995), which requires temperatures below the ice frost point ($T_{ice} \approx 188$ K in the lower stratosphere). However, NAT PSCs have been observed by both in-situ aircraft and satellite measurements in air masses that had not been exposed to temperatures below T_{ice} (e.g., Pagan et al., 2004; Larsen et al., 2004; Voigt et al., 2005; Pitts et al., 2011). Therefore, heterogeneous nucleation of NAT on meteoritic dust has been considered as an alternative "fast track" to NAT formation at temperatures above the frost point (Voigt et al., 2005; Hoyle et al., 2013). contrary to Biermann et al. (1996) who showed in laboratory experiments that heterogeneous nucleation rates on micrometeorites are too low to enhance freezing of PSCs above the frost point.

The uptake of chemical species, e.g. HCl, by PSC particles and the subsequent heterogeneous reaction rates depend on PSC particle composition and surface area density (and hence strongly on temperature). Chlorine reservoir species are converted into active chlorine species by heterogeneous reactions on the surface of PSCs through;

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \quad (1)$$

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \quad (2)$$

$$HOCl + H_2O \rightarrow Cl_2 + H_2O. \quad (3)$$

Although chlorine activation on PSCs is an essential step towards ozone depletion, under certain conditions the ozone loss may be rather insensitive to the rate constants of those heterogeneous reactions and thus to the composition of PSCs present (e.g., Drdla and Schoeberl, 2003; Wohltmann et al., 2013). For instance, this sensitivity is expected to be

589 small if the PSCs exist long enough so that one reaction partner of a heterogeneous reaction
590 becomes almost completely depleted. It is also small if one of the reaction partners has
591 already been depleted and its re-generation by gas-phase chemistry is slower than the
592 heterogeneous reactions.

593 According to the above-mentioned findings, the following questions are relevant for
594 understanding ozone depletion:

595 1) Which PSC compositions form under which conditions?

596 2) How sensitively do chlorine activation ~~and, consequently, ozone depletion~~ depend on
597 PSC composition?

598 In order to investigate Question 1, we used PSC observations by the CALIOP (Cloud-
599 Aerosol Lidar with Orthogonal Polarization) instrument on the CALIPSO (Cloud-Aerosol
600 Lidar and Infrared Pathfinder Satellite Observations) satellite in the Arctic winter 2009/2010
601 and temperature data from ECMWF (European Centre for Medium-Range Weather Forecasts)
602 analyses on backward trajectories initiated at the locations of the PSC observations. All three
603 PSC compositions mentioned above (STS, NAT, ice) were observed. These analyses show
604 that the PSC particle composition depends not only on the temperature at the time of the
605 observation, but also on the temperature history of the air parcel. This conclusion is in
606 agreement with the findings of Lambert et al. (2012), who used a similar approach with
607 CALIOP PSC composition and Aura Microwave Limb Sounder (MLS) HNO_3 data to analyse
608 PSC and HNO_3 evolution.

609 In order to study Question 2, we investigated the temporal evolution of HCl in the vicinity of
610 observed PSCs. For this, we calculated backward and forward trajectories from the positions
611 of the CALIOP PSC observations and considered Aura MLS HCl measurements within a
612 certain distance (”Match radius”) from those trajectories. The signature of chlorine activation
613 seen in the HCl data was compared to simulations from the Lagrangian chemistry-transport
614 model ATLAS (Wohltmann et al., 2010). ~~Additional runs of this model were carried out to~~
615 ~~estimate the sensitivity of chemical ozone depletion to different PSC compositions.~~

616 We concentrated on the time period of the first occurrence of PSCs during the winter (mid-
617 December 2009 – beginning of January 2010). This choice allowed us to rule out the prior
618 existence of PSCs and associated repartitioning of chlorine-containing species by

heterogeneous reactions. This winter was one of the coldest winters in the Arctic during the CALIPSO operation period when ice PSC was observed by the CALIOP measurements.

2. Data

2.1 CALIPSO/CALIOP PSC Data

CALIPSO, a component of the A-train satellite constellation (Winker et al., 2007, 2009), was launched in April 2006 into a 98.2° inclination orbit that provides extensive daily measurement coverage over the polar regions of both hemispheres up to 82° in latitude. CALIOP, the primary instrument on CALIPSO, measures backscatter at wavelengths of 1064 and 532 nm, with the 532-nm signal separated into orthogonal polarization components parallel and perpendicular to the polarization plane of the outgoing laser beam.

Pitts et al. (2007, 2009, 2011) developed a procedure for detecting PSCs using the CALIOP 532-nm scattering ratio (R_{532}, the ratio of total to molecular backscatter) and the 532-nm perpendicular backscatter coefficient. They further developed an algorithm to classify PSCs by composition based on the measured CALIOP aerosol depolarization ratio ($\delta_{aerosol}$, the ratio of perpendicular to parallel components of aerosol backscatter) and inverse scattering ratio ($1/R_{532}$). Pitts et al. (2009) defined four composition classes of PSCs, i.e., STS, ice, Mix 1, and Mix 2. Mix 1 and Mix 2 denote mixtures of liquid droplets with NAT particles in lower or higher number densities/volumes, respectively. Pitts et al. (2011) added two additional sub-classes of PSCs, i.e., Mix 2 enhanced, and wave ice PSCs.

In this study, we used three categories of PSCs from CALIOP data: STS, Mix (which includes Mix 1, Mix 2, and Mix 2 enhanced), and ice (which includes ice and wave ice) PSCs.

In order to assign PSC composition along the trajectories, we selected the composition of the CALIOP measurement location that was closest to each trajectory point on the same day. For each trajectory point, the horizontally closest CALIOP measurement profile was first determined and then the PSC classification closest in potential temperature to the trajectory point was taken from this measurement profile. An analogous method was used to produce the maps in Fig~~ure~~ 2.

Due to the sampling pattern of CALIOP, there is some intrinsic and unavoidable uncertainty in the PSC characterizations at any given location, which is typically some distance away from the point being measured by CALIOP. The approach we have used relies on the assumption that PSCs are sufficiently homogeneous on a spatial scale that corresponds to the average distance to the next measurement, which is about 100-200 km, and a time difference within 24 hours.

2.2 MLS Data

This study also uses data from the Microwave Limb Sounder (MLS) instrument on the Aura satellite (Waters et al., 2006). The Earth Observing System (EOS) Aura satellite was launched on 15 July 2004 and has been in operation since August 2004 making measurements between 82° N and 82° S. MLS measures millimeter- and submillimeter-wave thermal emission from the limb of Earth's atmosphere. We use MLS version 3.3 HCl, ClO, ~~HN~~O_3, and H~~O~~$_{3}$$_{2}$-O data (Livesey et al. 2006, 2013). Vertical resolution of MLS data is ~3 km in the lower stratosphere at 100-10 hPa. A discussion of the quality of MLS measurements can be found in Livesey et al. (2013). Error bars in the figures that follow indicate the 1σ precision of the measurements.

3. Analysis Method

3.1 PSC evolution in the northern winter 2009/2010

In the Arctic winter 2009/2010, PSCs started to appear in mid-December 2009 at around 23 km when the minimum temperature dropped below the nitric acid trihydrate saturation temperature T_{NAT} (Pitts et al., 2011). Figure 1 shows the temporal variation of the minimum temperature (T_{MIN}) between 50 and 90°N at the 30 hPa pressure level. ~~The thick black line is the mean over the winters 1978/79 to 2013/14, while the thin black lines are minimum and maximum temperatures. The thick red line shows the variation of the daily minimum temperature in the 2009/2010 Arctic winter.~~ The two green lines show the NAT and ice PSC

threshold temperatures (T_{NAT} and T_{ice}, respectively) calculated by assuming 6 ppbv of HNO_3 and 4.5 ppmv of H_2O. T_{MIN} dropped below T_{NAT} at the middle of December and below T_{ice} at the end of December 2009 and again in mid-January. A sudden stratospheric warming terminated the period with temperatures below T_{NAT} at the end of January 2010 (Dörnbrack et al., 2012).

The PSC observations of CALIOP are consistent with the temperature history in this winter. Figure 2a shows an example of the PSC field on the 550 K potential temperature surface for 21 December 2009 with CALIOP observation points, when substantial PSC coverage was first observed by CALIOP at this altitude (~23 km) in this Arctic winter. Global PSC field was created by selecting the closest CALIOP PSC measurement on the same day. Note that the CALIOP PSC products are only produced for nighttime orbit segments due to higher background lighting conditions during daytime. On 21 December 2009, the day/night transition occurs near 72°N. Also note that the area north of 82°N is shadowed by grey color, because there is no CALIPSO orbital coverage there. Similarly, Fig. ~~ure~~ 2b shows an example of the PSC field at 550 K for 1 January 2010, when the maximum extent of PSCs was observed at this altitude. PSC fields were created in this way for each day during the 2009/2010 Arctic winter.

3.2 Selection of trajectories for the case studies

As mentioned in Sect. ~~ion~~ 1, backward and forward trajectories from the positions of CALIOP PSC observations were calculated, in order to investigate the chemical effects of these PSCs by analysing chemical model runs and trace gas observations along these trajectories. In order to exclude any chemical effect of earlier PSCs in the analysed air masses, we concentrate on the time period of early winter (between 19 December 2009 and 3 January 2010).

As a first step, several cases of CALIOP observations of PSCs of a clearly defined composition class were selected. The selected cases encompass a range of different conditions with respect to temperature and PSC classification. Two examples are presented in Fig~~ure~~s. 3 and 4. In each case, a location in the center of such a PSC was selected. It was marked by a cross and a label in Fig. ~~ure~~ 3a ("n1": mix 1 PSC), and Fig. ~~ure~~ 4a ("e4": mix 2

enhanced PSC). In order to show the temporal evolution of temperature and HCl in the analysed airmass, 5-day backward and 5-day forward trajectories, starting at the marked position, were calculated. The corresponding trajectory model is taken from the ATLAS chemistry and transport box model (Wohltmann et al., 2010). Model runs are driven by meteorological data from the ECMWF ERA Interim reanalysis (Dee et al., 2011), with time resolution of 6h and horizontal resolution of 2 times 2 degrees. The vertical coordinate is potential temperature and vertical motion is driven by total diabatic heating rates from ERA Interim.

Figures 3b and 4b show MLS measurements of HCl along the path of the trajectories as a function of time (green dots with error bars). All HCl measurements that were closer than 200 km to the position of the trajectory at a given point in time are plotted. PSC occurrence is color coded in the background. Green shaded areas correspond to STS clouds, red shaded areas to NAT/STS mixture clouds, and blue shaded areas correspond to ice clouds. Grey areas correspond to sections of the trajectory north of 82°N, where no measurements from CALIOP or MLS are available. Nevertheless, we can find some matched MLS points within the grey area in Fig~~ure~~ 3b. This is because MLS observations were selected within a match radius of 200 km. Figures 3b and 4b show that HCl values were around 2 ppbv on the backward trajectories and that either no PSCs were measured by CALIOP or no measurements from CALIOP were available on the backward trajectory. HCl started to decrease near t=0, a time at which PSCs were present according to our choice of the trajectory starting points. Figures 3c and 4c show the temperature along the trajectories, with the PSC occurrence as in Figures 3b and 4b. The thin black lines correspond to T_{NAT} and $T_{NAT} - 3$ K, the thin blue line corresponds to T_{ice}. The threshold temperature for the formation of NAT clouds (T_{NAT}) is based on the equations of Hanson and Mauersberger (1988). For the forward part of the trajectory, HNO_3 and H_2O from the box model runs (cf. Sect~~ion~~ 4) were used for the calculation of T_{NAT}. For the backward part of the trajectory, HNO_3 and H_2O values were fixed at the starting values of the box model run. The threshold temperature for the formation of ice (T_{ice}) was calculated in the same manner from the equations of Marti and Mauersberger (1993). In the cases shown in Fig~~ure~~s. 3 and 4, the temperature does not drop below $T_{NAT} - 3$ K on the backward trajectory (before the occurrence of selected PSC). It can be seen that when temperature decreased, PSCs started to form along the path of the forward trajectory.

In order to analyse the temporal evolution of chemical species after the encounter of PSCs, ATLAS box model runs, which will be explained in the following Section in detail, will be performed on several trajectory cases. It is desirable to start these model runs from initial concentrations that have not been influenced by any earlier PSC occurrence in the airmass of interest. However, if these model runs started at the locations selected in the center of a PSC (as those marked in Fig~~ure~~s. 3a and 4a), then a part of the backward trajectory would lie within the selected PSC. Consequently, some chlorine activation might occur already before the beginning of the forward trajectory. In order to avoid this effect, the forward trajectories for the runs of the ATLAS box model are started before the encounter of the selected PSC. For this, a new starting point (corresponding to a new starting time t=0) of the trajectory calculations was selected on the original backward trajectory such that it fulfills the following conditions: (1) There is no PSC in the CALIOP data near the backward trajectory before the new starting time. (2) The temperature at and before the new starting time does not drop below T_{NAT} – 3 K. The assumption behind this is that a supersaturation of a factor of~~about~~ 10 (3 K supercooling) is needed for the formation of NAT clouds and that STS clouds only take up measureable quantities of HNO_3 below T_{NAT} - 3 K (Dye et al., 1992; Pitts et al., 2007). (3) The matched MLS HCl values at and before the new starting time were above ~2 ppbv, which proves that the airmass has not been processed by PSCs before the new t=0. In such a way, we selected ~30 trajectory cases in early winter between 19 December 2009 and 3 January 2010 for several PSC classes. Then we selected 11~~1~~ trajectories for case studies, which cover several different PSC composition classification and different temperature histories. The new trajectory starting points are~~(~~ summarised in Table 1.~~) for case studies.~~ Starting from these points, new 5-days forward and 5-days backward trajectories were calculated. ATLAS box model was run on these 5-days forward trajectories, which passed through the center part of the selected PSCs.

4. ATLAS model

4.1 Model description

The box model runs, simulating the temporal evolution of chemical species along the trajectories described in Sect~~ion~~ 3.2, use the chemistry box model of the ATLAS (Wohltmann et al., 2010). Updates to the chemistry model and PSC model are described in Wohltmann et al. (2013). The model includes a gas phase stratospheric chemistry module and heterogeneous chemistry on PSCs. It comprises 47 active species and more than 180 reactions. Absorption cross sections and rate coefficients are taken from recent JPL recommendations (Sander et al., 2011). The chemical model runs are driven by meteorological data from the ECMWF ERA Interim reanalysis (Dee et al., 2011).

The treatment of conditions where both NAT and STS PSCs are allowed to form in parallel, the model has changed compared to Wohltmann et al. (2013) to allow for more realistic behavior. In Wohltmann et al. (2013), only liquid clouds could form between T_{NAT} and the temperature corresponding to the assumed supersaturation for HNO_3 over NAT. At temperatures below that of the assumed supersaturation, NAT clouds would form first, usually consuming all available HNO_3 and impeding the formation of ternary liquid clouds (by chance, the temperature where binary liquid aerosols begin to take up HNO_3 in measurable quantities is about the same as the temperature where NAT clouds begin to form in the model). Since NAT/STS mixtures are commonly observed (e.g. Pitts et al., 2011), we implemented a simple algorithm that allows for mixed clouds: If the given supersaturation of HNO_3 over NAT is exceeded, only a predefined fraction of the amount of HNO_3 that has to be removed from the gas phase to reach the supersaturation again is allowed to go into NAT clouds. The remaining fraction is available for the formation of STS clouds. The fraction is set to 0.2 for our model runs.

~~**4.2 Sensitivity runs**~~

~~Three sensitivity runs with different assumptions on PSCs are performed for each trajectory. In the "STS+NAT" run, PSC information from CALIPSO is ignored and the box model forms PSCs according to temperature and available condensable HNO_3 and H_2O, in the same way as described in Section 4.1.~~

In the ATLAS model run~~this run~~, the NAT particle number density is set to 0.1 cm^{-3}, the ice particle number density is set to 0.01 cm^{-3}, and the STS droplet number density is set to 10

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826 cm^{-3}. A supersaturation of HNO_3 over NAT of 10 (corresponding to about 3 K supercooling)
827 is required for NAT particle formation. A detailed discussion of the rationale behind these
828 choices can be found in Wohltmann et al. (2013). For ice particles formation, a
829 supersaturation of 0.35 is assumed based on MLS satellite measurements of H_2O and
830 ECMWF temperatures. Reaction rates for NAT particles are based on scheme 1 in Carslaw et
831 al. (1997) and reaction rates for liquid particles are based on Hanson and Ravishankara (1994).

832 ~~The "STS" run is identical to the "STS+NAT" run, except that no NAT clouds are allowed~~
833 ~~to form.~~

834 ~~The "CALIPSO constrained" run uses the information from the CALIPSO satellite to~~
835 ~~constrain the formation of PSC within the model. Five different cases are considered:~~

836 ~~1. If CALIOP measures no PSCs, no clouds are formed in the box model runs.~~

837 ~~2. If CALIOP detects only STS, then STS is allowed to form according to temperature and~~
838 ~~species mixing ratios in the box model, as explained above. Note that in the "STS+NAT" and~~
839 ~~"STS" runs, STS may form outside of the area where CALIOP detects STS clouds, if the~~
840 ~~temperature conditions are appropriate. However, in the "CALIPSO constrained" run, the~~
841 ~~model will not form STS outside of the area where CALIOP detects STS. In addition, if~~
842 ~~CALIOP detects STS in a region where ECMWF temperatures are too warm for STS~~
843 ~~existence, the model will only produce binary liquid aerosol.~~

844 ~~3. If CALIOP detects mixed clouds, both STS and NAT clouds are simulated in the box~~
845 ~~model. STS clouds are simulated in the same way as above. NAT clouds are formed with a~~
846 ~~predefined number density of 10^{-3} cm^{-3} and a predefined radius of 2 µm.~~

847 ~~4. If CALIOP detects ice clouds, ice clouds are formed with a predefined number density of~~
848 ~~1 cm^{-3} and a predefined radius of 5 µm.~~

849 ~~5. There are no CALIOP measurements north of 82°N. In this region, the "CALIPSO~~
850 ~~constrained" run uses the same setting as the "STS+NAT" run.~~

851 ~~The NAT and ice cloud number densities used here were derived by comparing the 2-D~~
852 ~~histograms of CALIOP PSC observations (Figure 4 in Pitts et al., 2009) and theoretical~~
853 ~~calculation of NAT and ice PSC growth (Figures 5 and 6 in Pitts et al., 2009). Note that while~~

~~these numbers are plausible under atmospheric conditions, particles in the real atmosphere may exist over a wide range of sizes and number densities (e.g., Wegner et al., 2012).~~

4.2~~3~~ Chemical initialization

The model chemical initialization is performed in three steps. First, all of the species are initialized from the mixing ratio fields of an existing global model run of ATLAS for the winter 2009/2010 (the reference run in Wohltmann et al., 2013). For this, a short back trajectory is calculated from the starting position of each trajectory back to the time of the last model output of the global model run preceding the start date of the trajectory. The chemical model is then run forward on this short trajectory with the initialization taken from the nearest air parcel of the global model output.

In the second step, mixing ratio values for HCl, O_3 and H_2O are replaced by measurements from MLS. MLS gas-phase HNO_3 observations are not used, in order to avoid problems when some of the total available HNO_3 is in the condensed phase (the model needs total HNO_3 and MLS measures gas phase HNO_3). The MLS values for HCl, O_3 and H_2O are obtained by calculating a 5-day back trajectory from the starting point of each trajectory and calculating an average over all MLS measurements close to the trajectory (with a match radius of 200 km). In order to keep Cl_y (the sum of all inorganic species containing chlorine) constant at the value specified by the global ATLAS runs, the difference between the MLS HCl value and the HCl value of the global model run is added to (or subtracted from, depending on sign) the mixing ratio of $ClONO_2$. Note that no chlorine activation has yet taken place at the time when the model is initialized, and this correction does not produce negative $ClONO_2$ values for any of the trajectories.

In some cases (trajectories #05, #08, and #10), modelled $ClONO_2$ is fully depleted before HCl reaches the level indicated by the MLS measurements. In these cases, a third step is applied to ensure that HCl and $ClONO_2$ are adjusted such that the amount of HCl loss in the model matches the loss of HCl in the MLS data. In all of these cases, there is a significant difference between the observed HCl mixing ratios before and after the PSC occurrence. The magnitude of this observed drop in HCl is used as the initialization for $ClONO_2$, such that $ClONO_2$ is nearly depleted at the end of the box model run. In order to keep Cl_y constant

again, the difference between the new $ClONO_2$ value (taken from the decrease in observed HCl) and the old $ClONO_2$ value (after the first correction in the second step caused by MLS HCl) is added to (or subtracted from) ClO_x=ClO+2Cl_2O_2 in a way that preserves the partitioning between ClO and Cl_2O_2.

5. Results

5.1 Dependence of PSC classification on temperature history

In this section, we show the temporal change in PSC classification along eight~~nine~~ selected trajectories with different temperature histories.

Figures 5a-b~~e~~ show cases in which the airmass cooled gradually over a period of days to below T_{NAT} – 3 K. NAT/STS mixture PSCs started to appear when the airmass temperature decreased below approximately T_{NAT} – 4 K in all cases shown. No ice PSCs and only a negligible amount of STS PSCs were observed during the course of the trajectory. When temperatures warmed above T_{NAT}~~,~~ in trajectory case #1, the mixed PSCs mostly disappeared. Since there was no region within the polar vortex with temperatures below the frost point before these PSC events, the NAT/STS mixture PSC observed here was assumed to be formed without any prior exposure to ice PSCs.

Figures 6a-c show cases in which the airmass temperature decreased rather rapidly due to adiabatic cooling by orographic lift as it passed over Greenland. In these cases, STS formed first as the temperature decreased below approximately T_{NAT} – 4 K, followed by a transition to NAT/STS mixture PSCs as the temperature warmed to near T_{NAT}. When the temperature rose above T_{NAT}, the PSCs disappeared.

Figures 7a-c show cases where the airmass temperature decreased rapidly to T_{ice} due to adiabatic cooling by orographic lift as it passed over Greenland. In these cases, STS formed first as the temperature decreased below approximately T_{NAT} – 4 K, followed by the formation of ice as the temperature decreased to T_{ice}. As the temperature warms above T_{ice}, the ice PSC is transformed into a NAT/STS mixture PSC, as suggested by an old theory of NAT PSC formation (Koop et al., 1995). ~~With the exception of the #10 case, t~~The CALIOP ice PSC

observations coincide quite well with the trajectory segments when~~with~~ airmass temperatures cooled near~~below~~ T_{ice}. This proves the accuracy of ECMWF ERA Interim reanalysis temperature data to some extent even in a mesoscale scenario such as mountain-induced adiabatic cooling event. ~~However, as will be discussed later, our model runs suggest that the uncertainty in ECMWF temperature is about 1 K.~~

5.2 Comparison of MLS measurements with the ATLAS model

In this section, we show the temporal changes of several parameters modelled by ATLAS and compare these with Aura/MLS measurements.

Figure~~s~~ 8a-f~~i~~ show the trajectory case #03 that started at 07:58:21 UT on 23 December 2009. It is not known if PSCs existed between 8 and 49 hours after the starting time of the forward trajectory because the trajectory went into the polar region above 82°N latitude where there are no CALIOP measurements. At hour 49, the airmass encountered STS and then NAT/STS mixture PSCs as the temperature cooled below approximately T_{NAT} – 4 K as shown in Fig~~ure~~ 8a. The surface area densit~~y~~~~ies~~ of the PSCs calculated by ATLAS ~~for the three different sensitivity runs, i.e. the STS+NAT run, STS run, and "CALIPSO constrained run" are~~ is shown in Fig~~ure~~ 8b. ATLAS indicated a small increase in surface area density between days 1 and 2 when the temperature decreased approximately 4 K below T_{NAT}, where CALIOP was not able to measure in that period due to the sampling limitation stated above. ~~Similarly, the calculated heterogeneous reaction rate of $ClONO_2$ + HCl on the PSC particles is shown in Figure 8c. Note that the reaction rate decreased more rapidly than the surface area of the PSCs. This is due to the total loss of $ClONO_2$ as will be discussed later in detail.~~ Figure 8c~~d~~ shows the calculated and measured amount of HCl by ATLAS and by Aura/MLS, respectively. MLS observations were matched to the trajectory with a match radius of 200 km, as was explained in Sect~~ion~~ 3.2. When the temperature decreased to about T_{NAT} – 3 K, the calculated HCl started to decrease in all three model runs. Similarly, $ClONO_2$ started to decrease and was fully depleted between days 2 and 3 as is shown in Fig~~ure~~ 8d~~e~~. After this point, HCl could not decrease anymore because the reaction partner ($ClONO_2$) was already fully depleted. The measured and calculated HCl values agree quite well within the error bars of MLS measurements as expected. The depleted chlorine was converted into Cl_2 or ClOx as

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is shown in Fig. ~~ure~~ 8c~~f~~. Because little sunlight was present along the trajectory, only a small amount of ClOx exists in the form of ClO as is shown in Fig. ~~ure~~ 8f~~g~~ after day 4. ~~Figure 8h shows the calculated and measured amount of HNO_3 by ATLAS and by Aura/MLS, respectively. In the three different ATLAS model runs, different HNO_3 values were calculated. However, MLS HNO_3 values were much smaller than the modelled values in all three model runs after day 3. Since the denitrification module of the global ATLAS model is designed to work correctly only on larger spatial and time scales, it cannot reproduce the denitrification for a single trajectory correctly. Modelling HNO_3 correctly by ATLAS along individual trajectories is beyond the scope of this paper. Figure 8i shows the calculated and measured amount of O_3 by ATLAS and by Aura/MLS, respectively. Since there was not sufficient ClO available for catalytic ozone destruction due to the lack of solar illumination, both calculated and measured O_3 did not indicate any ozone depletion in this case.~~

Figure~~s~~ 9a-f~~i~~ show the trajectory case #05 that started at 17:53:38 UT on 30 December 2009. The trajectory encountered a region of CALIOP STS measurements after 10 hours as the temperature decreased below approximately T_{NAT} – 5 K. Between days 1 and 5, NAT/STS mixture PSCs were observed along the trajectory, as well as a very short period of ice PSCs between days 1 and 2 when the temperature cooled to T_{ice}. Calculated PSC surface area density increased rapidly when the airmass temperature decreased below around T_{NAT} – 3 K between days 0 and 2 as is shown in Fig. ~~ure~~ 9b. However, both HCl and $ClONO_2$ stopped decreasing just a few hours after the airmass encountered the STS PSCs, because the $ClONO_2$ was fully depleted within this time as is shown in Fig. ~~ures~~ 9c ~~d and 9~~and d~~e~~. The measured and calculated HCl values agree quite well. The depleted reservoir chlorine was first converted into Cl_2, then after exposure to sunlight (indicated by orange dots on the upper part of Fig. ~~ures~~ 9c~~d~~-f~~9i~~), Cl_2 was photolyzed to Cl which forms ClO_x (Fig~~ures~~. 9c~~f~~ and ~~9~~f~~g~~). The measured and calculated ClO values also agree quite well. ~~The temporal evolution of HNO_3 is shown in Figure 9h. The measured HNO_3 between days 2 and 5 is slightly depleted, suggesting the possibility of mild denitrification. A small amount of ozone depletion was modelled by ATLAS in this case when sufficient ClO was available as is shown in Figure 9i.~~

Figure~~s~~ 10a-f~~i~~ show the trajectory case #08 that started at 16:59:14 UT on 31 December 2009. After 3 hours, the airmass encountered STS PSCs as the temperature decreased below approximately T_{NAT} – 5 K. As the temperature further decreased to reach T_{ice} after 20 hours,

ice PSCs were observed by CALIOP as is shown in Fig.~~ure~~ 10a. When the temperature increased above T_{ice} after 23 hours, NAT/STS mixture PSCs were observed. This case is quite similar to the previous case. Calculated PSC surface area density rapidly increased when the airmass cooled to around T_{ice} between days 0 and 2 as shown in Fig.~~ure~~ 10b. However, both HCl and $ClONO_2$ stopped decreasing just a few hours after the airmass encountered STS PSCs, because $ClONO_2$ was fully depleted within this time as shown in Fig.~~ures~~ 10cd and ~~10~~de. Also in this case, the measured and calculated HCl values agree quite well. The depleted reservoir chlorine was first converted into Cl_2, then with exposure to sunlight (indicated by orange dots on the upper part of Fig~~ures~~. 10cd-~~10~~f~~i~~), Cl_2 was photolyzed to Cl which was then converted into~~form~~ ClO as shown in Fig.~~ure~~ 10fg. ~~The MLS HNO_3 values were slightly depleted between days 1 and 3, suggesting the possibility of a small degree of denitrification. In this case, slight ozone destruction was modelled by ATLAS when there was sufficient ClO available, as is shown in Figure 10i. However, the uncertainty in the measured ozone is too large to deduce a quantitative ozone loss amount.~~

5.3 Temperature sensitivity study for ATLAS model runs

Figure~~s~~ 11a-f~~i~~ show the trajectory case #02 that started at 08:09:30 UT on 21 December 2009. After 55 hours, the airmass encountered STS PSCs as the temperature decreased below $T_{NAT} - 4$ K for a while. Shortly afterwards, a mixed type PSC was observed by CALIOP. When temperature increased to around T_{NAT} at day 4, STS PSC was observed again before the airmass exited the PSC area. In this case, the time period when the temperature was below $T_{NAT} - 4$ K was relatively short as is shown in Fig.~~ure~~ 11a. As a result, the higher values of PSC surface area calculated by ATLAS were limited to a short time period at around day 2 as is shown in Fig.~~ure~~ 11b. As a result, the decrease of both HCl and $ClONO_2$ modelled by ATLAS was small, and $ClONO_2$ was not totally depleted even after passage through the PSCs. In addition, the ~~modelled HCl and $ClONO_2$ are very sensitive to different PSC scenarios that are assumed in this case. The STS+NAT model run produces the largest decrease in the chlorine reservoirs, while the CALIPSO-constrained model run produces the smallest~~

decrease in the chlorine reservoirs. Moreover, all three ATLAS model runs underestimates the loss of HCl compared with observations as is shown in Fig. ure 11cd.

In order to study the sensitivity of the ATLAS model runs to the ECMWF ERA Interim reanalysis temperatures, we made additional ATLAS model runs by introducing a ±1 K temperature bias. Figures 12a-fi show the same trajectory as Fig. ures 11a-fi with red and blue lines added to show the sensitivity runs with the temperature changed by ±1K, respectively. The reference run (black line) used no temperature biases.is the STS+NAT run. As is shown in Fig. ures 12b and 12e, a temperature change of only 1 K greatly affects the PSC surface area density and heterogeneous reaction rate of $ClONO_2$ + HCl. As a result, the modelled depletion of HCl and $ClONO_2$ are also significantly affected as is shown in Fig. ures 12cd and 12de. In fact, the minus 1 K model run result agrees fairly well with the MLS HCl observations as shown in Fig. ure 12cd. This result suggests the previous studies (e.g., Carslaw et al., 1994) that very accurate temperature data are required to correctly model the heterogeneous reactions on PSCs at temperatures near T_{NAT} – 4 K.

Figures 13a-fi show another example; trajectory case #09 which started at 18:35:15 UT on 31 December 2009. After 18 hours, the airmass encountered NAT/STS mixture PSCs as the temperature decreased below approximately T_{NAT} – 3 K. In this case, the time period when the temperature was below T_{NAT} – 3 K was very short (less than 10 hours), as is shown in Fig. ure 13a. Accordingly, the modelled increase of PSC surface area density and heterogeneous chlorine activation werewas very small as is shown in Fig. ures 13b and 13e. Consequently, the model did not produce substantial HCl or $ClONO_2$ depletion around day 1, as shown in Fig. ures 13cd and 13de. However, MLS HCl measurements do indicate some depletion between days 2 and 4, as shown in Fig. ure 13cd. These results again suggest the uncertainty of ECMWF temperature compared with the actual temperature.

Figures 14a-fi show the results of the temperature sensitivity study for case #09. As shown by Fig. ures 14b and 14e, perturbing the ECMWF temperature field by minus 1 K greatly increases the likelihood of PSCs around day 1. Consequently, the modelled HCl depletion for the minus 1 K case agrees with the MLS measurements quite well as shown in Fig. ure 14cd. This result again illustrates the importance of accurate temperature data especially when the temperature is around T_{NAT} – 4 K, which is the approximate threshold temperature of NAT/STS mixture and STS PSC formation.

6. Discussion

In Sect.~~ion~~ 5.1, we showed three typical temperature histories for PSC formation, i.e., gradual temperature decrease, rapid temperature decrease, and temperature decrease below T_{ice}. Figure~~s~~ 5a-b~~e~~ show the formation of NAT/STS mixture PSCs for the case of gradual temperature decrease in airmasses that have never experienced temperatures below T_{ice}. These cases clearly show the existence of an ice-free nucleation mechanism of NAT, as was previously suggested by Drdla et al. (2003), Larsen et al. (2004), Pagan et al. (2004), Voigt et al. (2005), Pitts et al. (2011), and Hoyle et al. (2013). The homogeneous nucleation of NAT in H_2O-H_2SO_4-HNO_3 solutions is kinetically strongly hampered and thus cannot be expected (Koop et al., 1997). One of the possible mechanisms for NAT formation is heterogeneous nucleation on solid particles such as meteoritic dust, as was postulated by Iraci et al. (1995), although Biermann et al. (1996) suggested that heterogeneous nucleation rates on micrometeorites are too low to enable freezing of NAT PSCs. Our results suggest the possibility of heterogeneous nucleation of NAT on solid particles as is already pointed out by Hoyle et al. (2013).

When the airmass temperature cooled rapidly due to adiabatic cooling by passage over mountain ranges, STS PSCs first formed as the temperature decreased below approximately $T_{NAT} - 4$ K as shown in Fig.~~ures~~ 6a-c. As the airmass temperature began to increase, a transition to NAT/STS mixture PSCs was observed without the existence of ice, especially for the case #06. Such a case was previously reported in PSC observations by backscatter sondes in the Arctic by Larsen et al. (1997). This result also indicates the possibility of ice-free formation of NAT.

Figure~~s~~ 7a-c show the cases when the airmass temperature decreased rapidly below T_{ice} due to adiabatic cooling over mountain ranges. As the airmass temperature began to increase, a transition to NAT/STS mixture PSCs was observed in all these cases. NAT/STS mixture PSCs usually disappear when the temperature warms above T_{NAT}. These cases are consistent with the ice-assisted nucleation mechanism of NAT suggested by Carslaw et al. (1995).

In Sect.~~ion~~ 5.2, comparisons of MLS HCl, ClO, ~~HNO_3,~~ and O_3 measurements with ATLAS model simulation results were shown for the trajectory cases #03, #05, and #08. Figure~~s~~ 8a-~~fi~~ shows the gradual temperature decrease case #03, Fig.~~ures~~ 9a-~~fi~~ shows the rapid temperature decrease case #05, and Fig.~~ure~~ 10a-~~fi~~ shows the temperature decrease below T_{ice} case #08. In all three cases, measured and modelled HCl and ClO agree fairly well~~, irrespective of the three model scenarios, i.e., "STS+NAT", "STS", and "CALIPSO constrained". The difference in modelled HCl and ClO among the three scenario runs was very small and it is difficult to tell which scenario most closely fits the measurements. In other words, if the airmass cooled below approximately T_{NAT} – 4 K for a longer time and consequently there was substantial chlorine activation on PSCs, the PSC classification has little impact on the details of the chlorine activation.~~ The chlorine activation usually occurred very rapidly within a few hours. The amount of HCl loss was shown to be limited by the available $ClONO_2$ amount. After all the $ClONO_2$ has been converted into ClO_x, HCl cannot be further depleted as previously shown in a model study by Müller et al. (1994).

In Sect.~~ion~~ 5.3, similar comparison results were shown for the cases #02 and #09, when the airmass temperature was below approximately T_{NAT} – 4 K for only a short time period. In these trajectory cases, the depletion of HCl and activation of ClO was underestimated by the model in comparison to the MLS measurements~~ for all three model scenarios, although the "STS+NAT" and "CALIPSO constrained" runs were closer to the measurements than the "STS" run.~~ In these cases, $ClONO_2$ was not totally depleted after passage through the PSCs. In cases where only a small amount of chlorine is activated, the amount of chlorine activation on PSCs is very dependent on ~~PSC classification and/or~~ airmass temperature. In fact, changing the ECMWF ERA Interim temperature field used as input to the ATLAS model by ±1 K has a large impact on the resulting magnitude of chlorine activation as shown in Fig~~ure~~s. 12a-~~fi~~ and 14a-~~fi~~. The large temperature sensitivity around T_{NAT} – 4 K can be attributed to the fact that both PSC surface area density and heterogeneous reaction probability (gamma value) increase quite rapidly around this temperature. Therefore, we conclude that quite accurate temperature knowledge is needed to correctly model the chlorine activation amount at around T_{NAT} – 4 K.

7. Conclusions

We performed trajectory analyses to study the evolution of PSC composition and chlorine activation from the reservoir species of HCl and $ClONO_2$. We investigated which PSCs form according to measurements of CALIOP as a function of the temperature history along the trajectories. We studied 11 individual trajectories in the early Arctic winter 2009/2010. In cases of a gradual temperature decrease below approximately $T_{NAT} - 4$ K, NAT/STS mixture PSCs appeared first. In these cases, ice PSCs were not observed by CALIOP before the formation of the mixed clouds, nor were temperatures below T_{ice} observed. This provides strong additional observational support for the conclusions by Drdla et al. (2003), Larsen et al. (2004), Pagan et al. (2004), Voigt et al. (2005), Pitts et al. (2011), and Hoyle et al. (2013) that NAT clouds can form without the prior formation of ice clouds. Since laboratory experiments suggest that homogenous freezing of NAT is unlikely, a possible mechanism of ice-free formation of NAT could be heterogeneous nucleation on solid particulates such as meteoritic dust (Voigt et al., 2005; Hoyle et al., 2013), although Biermann et al. (1996) suggested that heterogeneous reaction rates on micrometeorites are too low. When the airmass temperature dropped rapidly due to adiabatic cooling, STS PSCs formed first when the temperature decreased below approximately $T_{NAT} - 4$ K. If the temperature further decreased below T_{ice}, ice PSCs were formed. Then when the airmass temperature started to increase above T_{ice}, NAT/STS mixture PSCs were formed, as suggested by the formation pathway of NAT clouds from ice clouds (e.g. Carslaw et al., 1995).

We further analysed the chlorine activation process based on MLS observations of HCl and ClO and the ATLAS Chemistry and Transport Model runs. Several sensitivity runs with different temperature histories ~~or different PSC types~~ were conducted. We find that our cases fall in one of two categories.

(1) In most cases chlorine activation occurred sufficiently rapidly, such that the degree of chlorine activation by the first PSC encounter for the respective air mass was limited by the initially available $ClONO_2$, i.e. $ClONO_2$ concentrations fell to very low values. For these cases, ATLAS model results, i.e. the modelled mixing ratios of HCl and ClO_x before and after the chlorine activation by the PSCs, generally agreed well with the MLS observations. The good agreement is expected, since for these cases the degree of chlorine activation only

depends on available $ClONO_2$ and is largely insensitive to the rate of the heterogeneous reactions and therefore to the exact PSC ~~composition and~~ temperature. ~~This finding is further illustrated by the fact that all ATLAS sensitivity runs give very similar results for all these cases.~~

(2) In a few cases, temperatures during the first PSC encounter remained higher (around T_{NAT} − 4 K) and the chlorine activation is slower, such that the rates of the heterogeneous reactions integrated over the time of exposure to PSCs limit the degree of chlorine activation, rather than the available amount of $ClONO_2$. In these cases, substantial amounts of $ClONO_2$ can survive the initial PSC encounter and the model is not always able to reproduce the degree of chlorine activation. ~~As expected for these cases, the ATLAS sensitivity runs show that the amount of chlorine activation depends on both, PSC composition and temperature.~~ In particular, the sensitivity of chlorine activation to temperature is extremely large in these situations, suggesting that a temperature uncertainty of ±1 K is sufficient to explain the~~most~~ discrepanc~~y~~~~ies~~ between ~~model~~modelled and measured HCl amount ~~results and observations~~. However, based on the data from the winter 2009/2010 these situations are fairly rare. T_{NAT} − 4 K is an approximate threshold temperature for rapid chlorine activation on PSCs.

Author Contribution

H. N. and M. T. designed the method of this study. I. W. developed and ran the ATLAS box model, ran trajectory calculations, and developed the PSC interpolation algorithm. T. W., M. C. P., and L. R. P. developed and analysed PSC observations from CALIPSO/CALIOP data. M. L. S. developed and analysed minor species from Aura/MLS data. H. N, I. W., R. L., and M. R. discussed on the analysis results. H. N. prepared the manuscript with contributions from all co-authors.

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1402 Table 1. List of the selected cases for the trajectory runs. The first column shows the ID
1403 number of the case used in the following analysis, the second column shows the starting date,
1404 and the third column the starting time of the trajectory. The remaining columns show the
1405 location of the starting position (t=0) of the forward and backward trajectories.

1406

Case ID	Date	Time (UT)	latitude (N)	longitude (E)	altitude (km)	PT (K)	Pressure (hPa)
#01	2009/12/19	16:37:56	79.85	263.71	22.36	520.9	31.60
#02	2009/12/21	8:09:30	75.50	50.54	22.97	559.2	27.91
#03	2009/12/23	7:58:21	78.90	39.92	22.07	526.0	31.60
#04	2009/12/23	7:58:45	79.85	33.50	22.05	522.9	31.60
#05	2009/12/30	17:53:38	66.13	279.29	22.97	546.4	27.44
#06	2009/12/31	8:58:26	57.56	264.93	21.00	511.8	40.68
#07	2009/12/31	12:10:25	76.70	241.31	22.15	531.7	31.60
#08	2009/12/31	16:59:14	70.28	288.19	24.05	565.3	22.61
#09	2009/12/31	18:35:15	60.44	273.13	24.95	612.4	19.84
#10	2010/1/1	9:39:12	66.12	260.59	22.97	551.0	27.60
#11	2010/1/1	17:41:15	66.12	282.38	24.05	570.7	23.24

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1408
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Figure Captions

Figure 1. Variation of the minimum temperature (50-90°N) in the Arctic stratosphere at 30 hPa by Modern Era Retrospective-Analysis (MERRA) data. The thick black line shows the average minimum temperature between 1978/79 and 2013/14, while the thick and thin shaded area represents 30-70% and 10-90% percentile distributions, respectively. The red line shows the minimum temperature in the 2009/2010 Arctic winter. Two horizontal green lines represent the Type I (NAT) PSC threshold temperature assuming 6 ppbv HNO_3 and 4.5 ppmv H_2O, and the Type II (ice) PSC frost point temperature, respectively.

Figure 2. CALIOP PSC field for 21 December 2009 (a) and for 1 January 2010 (b) at the 550 K potential temperature surface. The green area represents STS PSCs, the red area mixed NAT and STS PSCs, and the blue area ice PSCs. Grey and black circles show CALIOP observation points for nighttime orbit segments. No measurements are available in the grey area around the pole (>82°N) due to the orbital coverage of the CALIPSO satellite.

Figure 3. (a) Time-altitude plot of the PSC distribution on 21 December 2009 from 13.09 to 13.30 UTC (fractional hours). PSC classifications are color coded (STS, M1: Mix 1, M2: Mix 2, M2e: Mix 2 enhanced, Ice, IceW: Wave Ice, for details see (Pitts et al., 2011)). The labels on the horizontal axis show fractional time, latitude and longitude. The cross with "n1" denotes the starting point of the forward/backward trajectories of panels (b) and (c) where mix 1 PSC was present. (b) HCl measurements by MLS (green dots with error bars) along 5 day forward and 5 day backward trajectories starting at the cross in panel (a). The match radius between MLS measurements and the trajectory is 200 km. The color coded areas show PSC occurrence measured by CALIOP along the trajectories, with the same color code as in Fig~~ure~~ 2. Time is given relative to the trajectory starting time. (c) Temperature along the trajectories (blue line). The thin black lines show the threshold temperature for NAT formation T_{NAT} and $T_{NAT} - 3$ K. The thin blue line shows T_{ice}.

Figure 4. Same as Fig.~~ure~~ 3 but for 2 January 2010 from 3.63 to 3.82 UTC. The cross with "e4" denotes the starting point of forward/backward trajectories where mix 2 enhanced PSC was present.

Figure 5. Temperature along the trajectories for the cases #01 (a) started at 16:37:56 UT on 19 December 2009 at altitude of 22.36 km, and~~,~~ #04 (b) started at 07:58:21 UT on 23 December 2009 at altitude of 22.05 km, as are ~~and #03 (c)~~ listed in Table 1. The color coded areas show PSC occurrence measured by CALIOP along the trajectories, with the ~~same~~ color code shown in lower left of panel (a).~~as in Figure 2.~~ Shaded grey area represents that PSC types were unknown due to the CALIPSO orbital limitation (>82° N). The thin black lines show the threshold temperature for NAT formation T_{NAT} and T_{NAT} – 3 K. The thin blue line shows T_{ice}.

Figure 6. Same as Fig.~~ure~~ 5 but for trajectory cases #05~~11~~ (a) started at 17:53:38 UT on 30 December 2009 at altitude of 22.97 km, #06 (b) started at 08:58:26 UT on 31 December 2009 at altitude of 21.00 km, and #11~~05~~ (c) started at 17:41:15 UT on 1 January 2010 at altitude of 24.05 km, respectively.

Figure 7. Same as Fig.~~ure~~ 5 but for trajectory cases #07~~8~~ (a) started at 12:10:25 UT on 31 December 2009 at altitude of 22.15 km, #08~~7~~ (b) started at 16:59:14 UT on 31 December 2009 at altitude of 24.05 km, and #10 (c) started at 09:39:12 UT on 1 January 2010 at altitude of 22.97 km, respectively.

Figure 8. Results of the ATLAS chemistry model along the trajectories and comparison with measurements by MLS for the trajectory case #03 starting ~~on 23 Dec. 2009~~ at 07:58:21 UT on 23 December 2009 at altitude of 22.07 km. (a) Temperature (as in Figs.~~ure~~ 5-7), (b) PSC surface area density, (c) ~~$ClONO_2$ + HCl heterogeneous reaction rate, (d)~~ HCl mixing ratio, (d~~e~~) $ClONO_2$ mixing ratio, (e~~f~~) ClO_x ($ClO + 2\times Cl_2O_2$~~)~~ + $2\times Cl_2$~~)~~ mixing ratio, (f~~g~~) ClO mixing ratio~~, (h) HNO_3 mixing ratio, and (i) O_3 mixing ratio~~. Matched MLS measurements of

HCl and, ClO, ~~HNO$_3$ and O$_3$~~ are shown in panels (cd) and, (fg), ~~(h) and (i)~~ (green dots with error bars). Black line in p~~P~~anels (b) to (f~~i~~) show ATLAS model results. ~~of the ATLAS chemistry model for the "STS+NAT" run (black curve), the "STS" run (grey curve) and the "CALIPSO constrained" run (blue curve).~~ The color coded areas show PSC occurrence measured by CALIOP along the trajectories, with the ~~same~~ color code shown in lower left of panel (b). ~~as in Figure 2.~~

Figure 9. Same as Fig~~ure~~ 8 but for trajectory case #05 starting at 17:53:38 UT on 30 December~~.~~ 2009 ~~at 17:53:38~~ at altitude of 22.97 km. The orange dots in panels (cd)~~-(~~f~~i~~) indicate the period of solar illumination when the solar zenith angle is smaller than 90 degrees.

Figure 10. Same as Fig~~ure~~ 8 but for trajectory case #08 starting at 16:59:14 UT on 31 December~~.~~ 2009 ~~at 16:59:14~~ at altitude of 24.05 km.

Figure 11. Same as Fig~~ure~~ 8 but for trajectory case #02 starting at 08:09:30 UT on 21 December~~.~~ 2009 ~~at 08:09:30~~ at altitude of 24.05 km.

Figure 12. Temperature sensitivity runs for trajectory case #02. The black line shows the standard~~"STS+NAT"~~ run, the red line a sensitivity run with temperature increased by 1 K and the blue line a sensitivity run with temperature decreased by 1 K. MLS measurements and PSC types are the same as in Fig~~ure~~ 11.

Figure 13. Same as Fig~~ure~~ 8 but for trajectory case #09 starting at 18:35:15 UT on 31 December~~.~~ 2009 ~~at 18:35:15~~ at altitude of 24.95 km.

Figure 14. Temperature sensitivity runs for trajectory case #09. Line colors here are the same as those in Fig. 12.

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