

Reply to reviewer #1

We thank anonymous **reviewer #1** for his/her constructive review that would improve the contents of our paper. The review comments by anonymous **reviewer #1** are numbered and repeated below as *in italic letters*, followed by our answers. In the new draft with corrections (supplement file), **red**, **purple**, and **blue** corrections are the revisions suggested by **reviewers #1**, #2, and #3, respectively. **Yellow-marked sentences** were also added in response to Short Comment #1 by Dr. Adrian Tuck.

GENERAL COMMENTS

(1) More context for the FTIR data should be given. A few questions come to mind.

- Is this the first time that the Syowa FTIR data has been retrieved/written up? Or are there other papers that describe this instrument and the data?

Yes, this is the first time that the Syowa FTIR data were retrieved and submitted to a journal paper.

(2) - Why is there only 2007 and 2011 data? Was the instrument not deployed in other years?

The FTIR was installed at Syowa Station in March 2007, and we made one year of operation in 2007. After that time, there were no one who could operate the FTIR at Syowa Station. In 2011, another FTIR operator wintered at Syowa Station, and made one year of FTIR operation. Then, after a few more operation in 2016, the FTIR was brought back to Japan in 2017. This sequence was now apparently described in Section 2.1.

(3) - Are the data publicly available?

Yes, we put the Syowa FTIR data in our data repository of our institute and put DOI information for them. The MIROC3.2 CCM results are stored at the CCMI site of BADC. This information was described in the “Data availability” now.

(4) - How to these data fit in with other ground-based FTIR datasets collected at high latitudes? Is the data quality similar? Have other FTIR instruments been used to study trace gases during spring-time ozone depletion?

As far as we know, there have been only two other FTIR instruments in Antarctica. One is at South Pole Station (90°S), and the other is at New Zealand’s Scott Station in Antarctica. We added description related to South Pole FTIR in Section 2.1. The data quality should be similar. However, due to the location of Scott Station (78°S), they cannot measure solar infrared spectra until September when ozone hole is already in progress. I don’t know any publications which focused spring-time ozone depletion using the other stations’

FTIR data so far. Therefore, the Syowa Station's FTIR has an advantage to study ozone-hole-related issues.

(5) The validation sections should be more specific in terms of how validation methods are applied (see specific comments for details). It would also be useful to answer:

- What is the expected uncertainty in the FTIR measurements? Is this something you retrieve?

We added typical retrieval error of each species in old Table 2 (new Table 1).

(6) - How do your validation results compare with validation of other ground-based FTIR instruments? Is the instrument at Syowa performing similarly to other FTIR?

By comparing our results with other FTIR validation results by Schneider et al. (2008), they look very similar. We described this issue in Section 3.

(7) - Are there any other factors that could affect comparison results? Do any of these species vary diurnally? Is there a chance that the satellite and station are measuring very different air masses (e.g., inside/outside the vortex) for some coincidences? If either of these are factors, how does this affect interpretation of the data in Sect. 4?

Among the chemical species we analyzed, only ClO has diurnal variation. Therefore, we used only daytime ClO data for the analysis. Although we set relatively strict collocation criteria (within 300 km radius and +/- 6 hours) for validation, there is a chance that satellite and station are measuring rather different airmasses when Syowa Station was located near the polar vortex edge. In order to check whether such a situation occurs or not, we looked at equivalent latitudes (EL) of measurement locations of MLS and Syowa Station for the collocated coincidence pairs. The result is shown in Figure A (below). As a result, differences of EL are always within 10 degrees in all cases. We now picked up the collocation pairs whose difference in EL are within +/- 5 degrees. The results are shown in Figures B and C (below). As you can see in these figures, the comparison results show almost similar features. Therefore, we concluded that the difference in EL within 10 degrees does not affect the validation results.

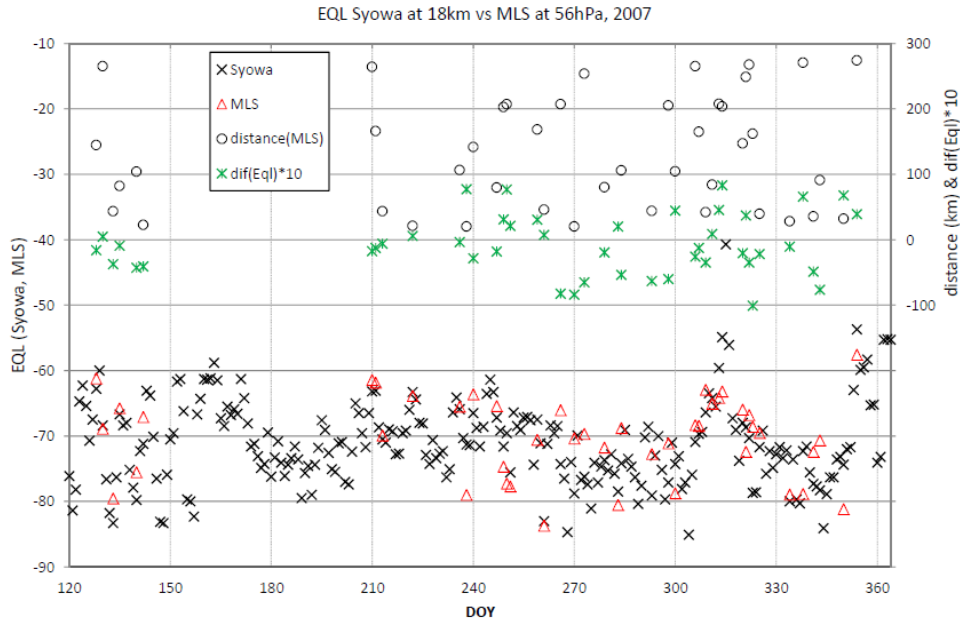


Figure A. Equivalent latitudes (EL) of Syowa Station (black crosses) at 18 km, EL of MLS (red triangle) at 56 hPa, distance between Syowa and MLS measurement locations (black circles), and differences in EL (green crosses) in 2007. Note that the values of differences in EL are multiplied by 10.

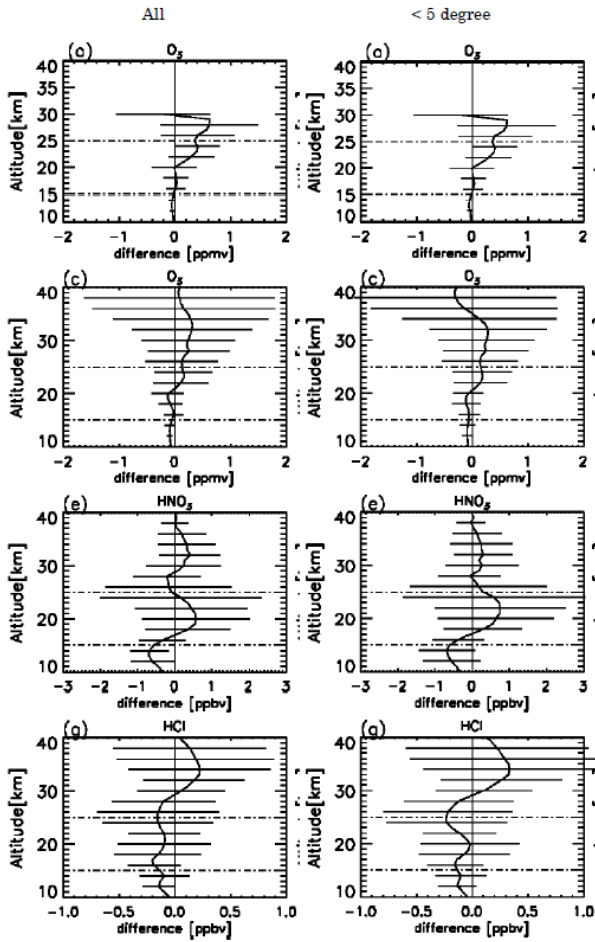


Figure B. Absolute differences with all collocation pairs (left columns) and those for differences in EL < 5 degrees (right columns).

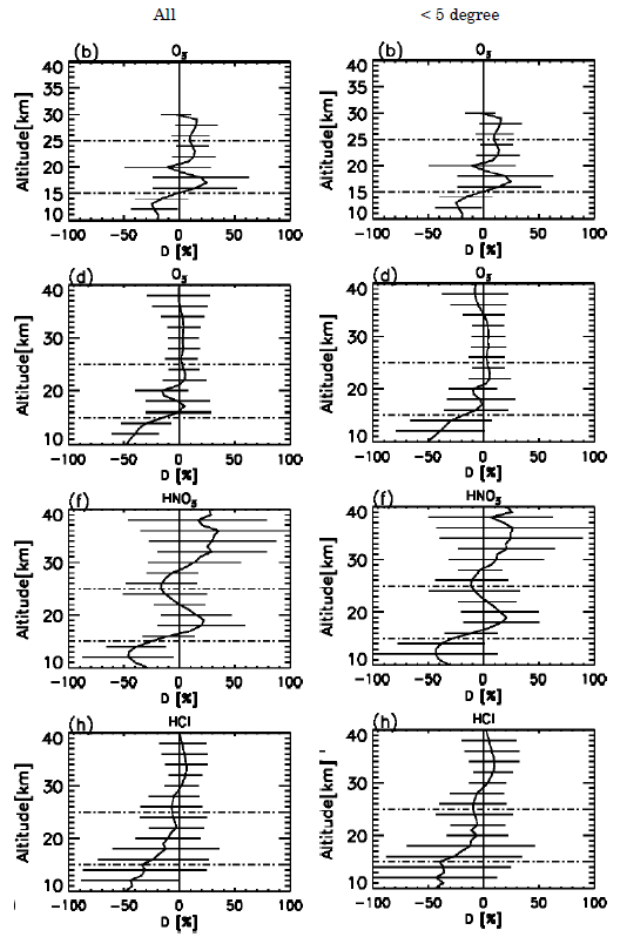


Figure C. Percentage differences with all collocation pairs (left columns) and those for differences in EL < 5 degrees (right columns).

(8) The discussion of results is repetitive and at times is difficult to follow. There are many timeseries figures (Fig. 4-9; Fig. 11-12). I found it hard to track through these and determine what exactly the authors were trying to highlight. I also had a hard time connecting all of these pieces to the concluding arguments around transport, chlorine deactivation, etc. A few possible solutions:

- Determine what you are trying to show, perhaps starting from the statements made in the conclusion. Only include figures/discussion that are relevant to what you're trying to show. Move additional timeseries figures into an appendix or supplement. Some tables (Table 1, Table 4) could also be moved out of the main body of the paper.

We modified several descriptions in Sections 4. Table 1 is now moved to Appendix, and Table 4 was deleted from the draft.

(9) - For Fig. 8-9 is there a more concise way of showing the relationships between the chlorine species than using the timeseries (e.g., through scatter plots or something else)?

We modified Figures 8 and 9. Now, partitioning of chlorine species are expressed by bar graphs instead of scatter plots in order to gain visibility. Also, descriptions of these figures were modified accordingly in Section 4.2.

(10) - Can the comparison with the modelling data be merged in with the validation of the FTIR (Sect. 3)? Can the modelling timeseries figures be folded into the timeseries figures presented in previous sections?

We showed modelling data in order to show other chlorine species which cannot be measured by FTIR and/or satellites, not for validating our measurements. Model data validation is out of the focus of this paper. Therefore, the modelling data section is kept as it is.

(11) I found it hard to follow the discussion around the mechanisms behind the decrease of HCl. It would be helpful if the discussion was expanded, to help answer the following:

- What hypotheses are there for the decrease in HCl in the literature? Is there just Solomon et al. (2015) and Grooss et al. (2018)? Are these hypotheses in conflict with each other or is it possible that they both contribute to the decrease in HCl together?

Also, there was several comments by reviewer-#3 on the decrease of HCl. The discussion on the decrease of HCl is much expanded. In the current modified manuscript, we showed two hypotheses in parallel; one is the ClONO₂ transport from the sunlit lower latitude towards the core of the vortex based on Solomon et al. (2015), and the other is the heterogeneous reaction between HCl and HOCl based on Müller et al. (2018). Please see the revised Section 4.6.

(12) - For the existing hypotheses, what data/evidence were used to develop the hypotheses? How does the data that you collected add to the existing supporting data/evidence?

The main data we used are based on our MIROC3.2 CCM results. However, our measurements of ClO, HCl, and ClONO₂ gains insights for these hypotheses.

(13) - Why does the sporadic increases in ClONO₂ in the model data support the transport mechanism? Do you have any other data to support that ClONO₂ is being transported (e.g., maps of ClONO₂, tracers showing transport patterns, evidence in the satellite data)? Are there alternative mechanisms that could explain your observations, such as chemistry?

Although there was no direct evidence of ClONO₂ transport, if ClONO₂-rich airmass was transported from the vortex boundary towards the vortex core region, it could decrease HCl by heterogeneous reaction (R1). Another alternative mechanism to decrease HCl was the heterogeneous reaction with HOCl (R4), which is now shown by another increase pattern on July 7 (day 188) and July 20 (day 201) in Figure 15(e).

(14) - Can your data be used to refute any other hypotheses for decreasing HCl?

Our data are consistent with both ClONO₂ transport hypothesis and reaction with HOCl hypothesis.

SPECIFIC COMMENTS:

(15) - Page 1, Line 17: You state “This was the first continuous measurements of chlorine species throughout the ozone hole period from the ground in Antarctica” here and elsewhere in the paper. This statement is a bit vague. Have other studies looked at any chlorine species from the ground in Antarctica? Are they looking at fewer species? Or for shorter time periods? It would be helpful if you included a literature review of ground-based measurements (FTIR and maybe other measurements of chlorine, such as OClO from UV-vis?) in Antarctica in your introduction.

We now described history of several ground-based observations except for FTIR (UV-visible and microwave) related to ozone chemistry in the last paragraph of Section 1, and the history of Antarctic ground-based FTIR measurements in the first paragraph of Section 2.1. Other FTIR stations in Antarctica can measure ozone-related species only after September, when ozone hole was at the recovery phase. This was now described in Section 2.1.

(16) - Page 4, Line 25: Are there other ground-based FTIRs in Antarctica?

Yes, there were two other ground-based FTIRs in Antarctica in history; one at South Pole Station, and the other

at McMurdo/Scott Station, which is now described in Section 2.1. We think the South Pole FTIR is not in operation now.

(17) - Page 5, Line 1: What is the temporal resolution of the FTIR at Syowa? Does it only take measurements during sunny days? Does it require manual operation?

One measurement takes about 10 minutes and we can make observations only on sunny days. It requires manual operation. This was explained in Section 2.1 now.

(18) - Page 5, Line 18: Is there a way of using the averaging kernel to determine whether the 18 km and 22 km concentrations are independent from each other?

The concentrations of 18 km and 22 km are expected to be almost independent when you look at the averaging kernel in Figure 1 and the degree of freedoms (DOFS) in new Table 1.

(19) - Page 5, Line 25: State where various satellite datasets were obtained from? (E.g., URL?)

We now showed the URLs of satellite dataset pages.

(20) - Page 5, Line 24: The application of selection criteria should be clarified, perhaps with a full paragraph at the end of this section. Was this same criteria applied to all three satellite instruments (MLS, MIPAS, and CALIPSO)? Was the same criteria used for both the validation (Sect. 3) and the discussions of results over Syowa (Sect. 4)? E.g., for the timeseries figures was the 6 h criterion applied?

The selection criteria for MLS and MIPAS are already stated in the draft (within 300 km radius from Syowa Station and within +/-6 hours of the FTIR measurement). The same criteria were used both for the validation and the results. For the CALIPSO data, we selected the closest orbital data of the day, whose maximum distance to Syowa Station is 320 km. This is now stated in the draft.

(21) - Page 5, Line 30: Have you considered applying a selection criteria based on inside/outside the polar vortex to the satellite data along their line of sight instead of using values over the station for all measurements?

No. As is stated in (old draft's) page 6, line-16, we collocated the locations of tangent height of 20 km for the direction of the sun from Syowa Station at the time of the FTIR measurement, and the tangent point at 20 km for the satellites' data.

(22) - Page 6, Line 18: What is the shape of the 5 km-wide slit function? Is this based on the FTIR resolution? Why was this used instead of the averaging kernel? Also, why are the MLS data smoothed? Is the vertical

resolution for MLS much higher than the ground-based FTIR?

It is a 5 km-wide running mean. The description was reworded. 5 km is the typical vertical resolution of FTIR measurements. Since the vertical resolution of satellite measurements are a bit better than FTIR resolution (3-4 km for MLS, and 3 km for MIPAS), smoothing of ozonesondes and satellites' data were performed in order to merge the vertical resolution of each measurement.

(23) - Page 6, Line 25: State the expected uncertainty and any expected biases in ozonesonde measurements

Typical precision and accuracy of the ECC-type ozone sondes are considered to be $\pm(3-5)\%$ and $\pm(4-5)\%$, respectively (Komhyr, 1986). This is now described in the second paragraph of Section 3.

(24) - Page 6, Line 24: I'm a bit confused about the language used throughout this section. The figures show mean relative difference and mean absolute difference versus altitude. Replace "The absolute difference. . ." with "The mean absolute difference. . ." and "The mean relative difference" in this line.

We now added the word "mean" at several places in Section 3. Also, "mean absolute difference" was used instead of "agreement" at several places for clarity.

(25) - Page 6, Line 25: What do you mean by "mean relative difference" here? Is this the mean relative differences averaged again over an altitude range? It might be simpler just to state the mean relative difference values at 18 km and 22 km instead of taking another average over altitude.

First, altitude range is different (15-25 km) and (18-22 km). Second, the "averaged" value in 18-22 km range was calculated. We rewrote "the average of mean relative differences ..." here.

(26) - Page 6, Line 26: What to you mean by "within error bars"? Are you referring to the standard deviation in the mean differences? This isn't really an error – it's the variability in the comparisons. It would make more sense to determine whether the agreement is as expected based on estimated uncertainty in the FTIR measurements (if this exists) and known uncertainties/biases in the satellite data. Also, why is the standard deviation used for the comparisons instead of the standard error?

The typical errors in FTIR measurements are shown in (new) Table 1 (old Table 2). We added some more official error values of satellite measurements in Section 3. We now used standard root mean square errors of FTIR and validation data instead of standard deviation, and rewrote to: "FTIR data agree with validation data within root mean squares of typical errors in FTIR and validation data at the altitude of interest." Also, the figure caption in Figure 2 had a mistake. We now rewrote to: "Horizontal bars indicate the root mean squares of differences at each altitude." Root mean squares of official errors in FTIR and satellite measurements are now added in (new) Table 2 (old Table 3).

(27) - Page 6, Line 31 – Page 7, Line 2: *See comments for previous paragraph.*

Same as above.

(28) - Page 7, Line 10: *“with a precision of 0.2-0.6%” – is this the precision in the MLS measurements? Or is this the precision of the systematic bias?*

It was a precision in the MLS measurements, but not 0.2-0.6%, but 0.2-0.6 ppbv, which corresponds to 10-30 % (See Table 3.9.1 in Livesey et al., 2013). We corrected the description here.

(29) - Page 8, Line 6: *You describe a set of steps for detecting the inner and outer edges of the vortex. Is this a new method? Is this expected to work better than other established methods for some cases?*

When we looked at the actual variation of the isentropic potential vorticity gradient with respect to equivalent latitude, we often saw apparent double-peak structure of polar vortex boundaries at 500-600 K in the case of Antarctic winter (see Figure 5 in Tomikawa et al. (2015)). Therefore, we decided to determine the inner and outer edges of the vortex when there were double peak structures. Actually, this method seems to work better with interpreting the observed data related to polar chlorine chemistry, rather than the conventional single vortex boundary categorization (e.g., Nash et al. 1996). This description was now added in the text.

(30) - Page 8, Lines 11-14: *Please break this down into smaller steps – I have a hard time understand what was done. My best guess is that you calculated the isentropic potential vorticity gradient as a function of equivalent latitude. You found the local maxima. You defined the inner/outer edges of the vortex at the local maxima that both (?) exceeded the wind-speed threshold and were at least 5 in equivalent latitude apart? Are there always only two local maxima that meet these criteria?*

Your understanding is correct. When there was only one local maxima, the regions are categorized into only two categories (inside and outside the polar vortex, i.e., no boundary region). In order to describe the definition of polar vortex boundaries in more detail, the polar vortex boundary definition part was now moved to Appendix B, and new Figures A1 and A2 were added.

(31) - Page 8, Line 18: *Did you filter the MLS data according to an error threshold? Or did you just remove suspect data when you looked at the timeseries? All filters applied to the satellite data (for, e.g., uncertainty, etc) should be described explicitly in Sect. 2.2.*

The lack of ClO and HCl data from day 195 to 219, 2007 is due to extremely large error values in the MLS data products (~1.2 ppbv error compared with ~0.2 ppbv error in other periods). The lack of ClONO₂ data from day 170 to 216, 2007 are negative values (-999.9) in MIPAS data products. This was now described in

the text.

(32) - Page 11, Lines 10-24: Can the model comparisons be merged into Sect. 3? It would be nice if consistent comparison methods were applied. Similar to Sect. 3 – are the comparisons consistent with what is expected based on known model performance and known biases in the satellite instruments?

We showed modelling data in order to show other chlorine species which cannot be measured by FTIR and/or satellites, not for validating our measurements. Model data validation is out of the focus of this paper. Therefore, the modelling data section is kept as it is.

(33) - Page 11, Line 28: Why was a different method used to determine the polar vortex than at Syowa station?

We now unified the method of polar vortex definition at Syowa Station. The definition method of polar vortex boundaries is now moved to Appendix B. The description of polar vortex boundary in Section 4.5 was modified.

(34) - Page 11, Line 31: What do you mean by “This boundary was located in between the inner and the outer edge of the polar vortex as were defined in Sect. 4.1”? Did you compare the two definitions of the vortex? If so, was this just done at Syowa station for all data or a subset of data? Or is it the case that the max gradient of PV at 475 K is always between the inner/outer edge values by definition?

Now the definitions of polar vortex boundary were unified.

(35) - Table 4: Should describe how you came up with each of the various ranges presented in the table. Here are a few examples of questions that should be answered. How do you define the threshold for a ClONO₂ enhancement or ozone starting-ending day of decrease? What are given in “HCl Value after increase” ranges? Is this the min/max of individual FTIR measurements over a given time-period? For the ClO enhancement period, is the 80% of maximum value different in 2007 and 2011 or is a single value used? What does “Variation when HCl 0 ppbv” mean?

We thought this table can be used by readers to see typical values of each species during the development and recovery of ozone holes in 2007 and 2011. However, it is rather arbitrary to pick up each value. Moreover, the contents of this table are not discussed in the paper. Therefore, we decided to omit this table from our paper.

(36) - Figure 3: Can you add a panel describing hours of sunlight or SZA here or to one of your other timeseries? It would be helpful to visualize this through discussions around available sunlight.

We added a panel for showing daytime hours in Figure 3(a).

(37) - Figure 3: Are the gaps in the PSC timeseries because CALIPSO observed no PSCs or because CALIPSO didn't collect any coincident data during this time? Either describe in text and/or add marker for CALIPSO measurements which did not observe PSCs.

The gaps in the PSC timeseries are the days when CALIPSO observed no PSCs over Syowa Station. We looked at the closest CALIPSO orbit to Syowa Station in each day. This daily sampling is now described in the last paragraph of Section 2.2.

(38) - Figures 14/15: Why have you used model data instead of satellite data for the parameters that are available from satellite? Did you check to see if the satellite saw the same patterns as the model?

The comparison between satellite observations and model results were shown in Figures 11 and 12, although comparison or validation of model results with actual measurements are not the main issue of this paper. In Figures 14 and 15, we focused on MIROC3.2 model results, in order to keep the consistency of each chlorine species.

MINOR/TECHNICAL COMMENTS:

(39) - Throughout the text, there are some awkwardly worded sentences and minor grammatical mistakes. I assume that these would be corrected through copy-editing, so have not listed these here, unless the meaning is unclear.

We think grammatical mistakes will be corrected through copy-editing.

(40) - Table 2: Define "PT"

We reworded to "Pressure and temperature profiles".

(41) - Table 3: Should define the fields included in the table. Is D(%) 18-22 km the average of the mean relative differences? Is (Min/Max %) 18-22 km the max/min mean relative difference across the various altitudes? (Might be better just to show mean relative differences +/- standard error at 18 km and at 22 km.)

Yes, your understanding is correct. We modified (new) Table 2 (old Table 3) to explain the validation results more comprehensively. The numbers in this table are now explained in the text in Section 3 as well.

(42) - Table 3: See comment re: precision in Page 7, Line 10

It was modified in the (new) Table 2 (old Table 3).

(43) - Table 3: Replace “Agreement” with “Range of mean absolute differences for 15-25 km”

It was replaced as suggested.

(44) - Figure 2, caption: Replace “Absolute (a) and percentage” with “Mean absolute (a) and mean percentage”

They were replaced as suggested.

(45) - Figure 2, caption: Replace “FTIR measurements and those from ozonesonde” with “FTIR measurements minus those from ozonesonde”

They were replaced as suggested.

(46) - Figure 2, caption: Move “Horizontal bars indicate the standard deviation of differences at each altitude.” to the end of the caption, since it applies to all panels.

It was moved as suggested.

(47) - Figure 2, caption: Describe what the horizontal dashed lines indicate.

They indicate the altitude range of our focus (15-25 km). We also described it at the last paragraph of Section 2.1.

(48) - Figure 4, caption: Replace “from N_2O value” with “from Aura/MLS N_2O ”.

It was replaced as suggested.

Chlorine partitioning near the polar vortex ~~edge~~**boundary** observed with ground-based FTIR and satellites at Syowa Station, Antarctica in 2007 and 2011

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Abstract.

We retrieved lower stratospheric vertical profiles of O₃, HNO₃, and HCl from solar spectra taken with a ground-based Fourier-Transform infrared spectrometer (FTIR) installed at Syowa Station, Antarctica (69.0°S, 39.6°E) from March to December 2007 and September to November 2011. This was the first continuous measurements of chlorine species throughout the ozone hole period from the ground in Antarctica. We analyzed temporal variation of these species combined with ClO, HCl, and HNO₃ data taken with the Aura/MLS (Microwave Limb Sounder) satellite sensor, and ClONO₂ data taken with the Envisat/MIPAS (The Michelson Interferometer for Passive Atmospheric Sounding) satellite sensor at 18 and 22 km over Syowa Station. HCl and ClONO₂ decrease occurred at both 18 and 22 km, and soon ClONO₂ was almost depleted in early winter. When the sun returned to Antarctica in spring, enhancement of ClO and gradual O₃ destruction were observed. During the ClO enhanced period, negative correlation between ClO and ClONO₂ was observed in the time-series of the data at Syowa Station. This negative correlation was associated with the [relative](#) distance between Syowa Station and the ~~inner~~ edge of the polar vortex. We used MIROC3.2 Chemistry-Climate Model (CCM) results to see the comprehensive behavior of chlorine and related species inside the polar vortex and the ~~boundary~~**edge** region in more detail. From CCM model results, rapid conversion of chlorine reservoir species (HCl and ClONO₂) into Cl₂, gradual conversion of Cl₂ into Cl₂O₂, [increase of HOCl in winter period](#), increase of ClO when sunlight became available, and conversion of ClO into HCl, was successfully reproduced. HCl decrease in the winter polar vortex core continued to occur due to [either](#) the transport of ClONO₂ from the subpolar region to higher latitudes, providing a flux of ClONO₂ from more sunlit latitudes into the polar vortex [or the heterogeneous reaction with HOCl](#). Temporal variation of chlorine species over Syowa Station was affected by both heterogeneous chemistry related to Polar Stratospheric Cloud (PSC) occurrence ~~deep~~ inside the polar vortex, and transport of an NO_x-rich airmass from ~~lower latitudinal~~**the** polar vortex boundary region which can produce additional ClONO₂ by reaction

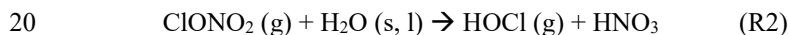
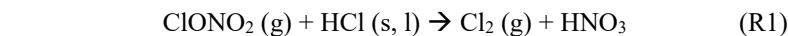
of ClO with NO₂. The deactivation pathways from active chlorine into reservoir species (HCl and/or ClONO₂) were ~~confirmed~~^{found} to be highly dependent on the availability of ambient O₃. At an altitude where most ozone was depleted in Antarctica (18 km), most ClO was converted to HCl. However, at an altitude where there were some O₃ available (22 km), additional increase of ClONO₂ from pre-winter value can occur, similar to the case as in the Arctic.

5

1. Introduction

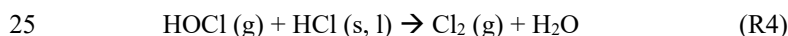
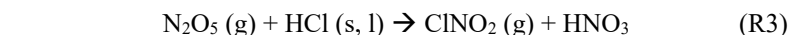
Discussion of the detection of “recovery” of the Antarctic ozone hole as the result of chlorofluorocarbon (CFC) regulations has been attracting attention. The occurrence of the Antarctic ozone hole is considered to continue at least until the middle of this century. The world’s leading Chemistry-Climate Models (CCMs) indicate that the multi-model mean time series of the springtime Antarctic total column ozone will return to 1980 levels shortly after mid-century (about 2060) (WMO, 2019). In fact, the recovery time predicted by CCMs has large uncertainty, and ~~the~~^{the} observed ozone hole magnitude also shows year-to-year variability (~~e.g., see Figure 4-6 in WMO (2019)).~~^{e.g., see Figure 4-6 in WMO (2019)).} Although Solomon et al. (2016) and de Laat et al. (2017) reported signs of healing in the Antarctic ozone layer only in September ~~month~~, there is no statistically conclusive report on the Antarctic ozone hole recovery (Yang et al., 2008; Kuttippurath et al, 2010; WMO, 2019).

To understand ozone depletion processes in polar regions, understanding of the behavior and partitioning of active chlorines (ClO_x=Cl+Cl₂+ClO+ClOO+Cl₂O₂+~~HOCl+ClNO₂~~) and chlorine reservoirs (HCl and ClONO₂) are crucial. Recently, the importance of ClONO₂ was reviewed by von Clarmann and Johansson (2018). Chlorine reservoir is converted to active chlorine that destroys ozone on polar stratospheric clouds (PSCs) and/or cold binary sulphate through heterogeneous reactions:



where g, s, and l represent the gas, solid, and liquid phases, respectively (Solomon et al., 1986; Solomon, 1999; Drdla and Müller, 2012; Wegner et al., 2012; Nakajima et al., 2016).

Heterogeneous reactions:

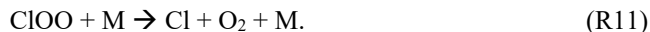


are responsible for additional chlorine activation. When solar illumination is available, Cl₂, HOCl, and ClNO₂ are photolyzed to produce chlorine atoms by reactions:

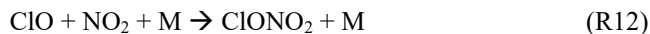


The yielded chlorine atoms then start to destroy ozone catalytically through reactions (Canty et al., 2016):





There are three types of PSCs, i.e., nitric acid trihydrate (NAT), supercooled ternary solution (STS), and ice PSCs. When the stratospheric temperatures get warmer than NAT PSC saturation temperature (about 195 K at 50 hPa) and no PSCs are present, deactivation of chlorine starts to occur. Re-formation of ClONO_2 and HCl mainly occurs through reactions (Grooß et al., 2011; Müller et al., 2018):



The re-formation of ClONO_2 by reaction (R12) from active chlorine is much faster than that of HCl by reactions (R13) and (R14), if enough NO_x are available (Mellqvist et al., 2002; Dufour et al., 2006). But the formation rates of ClONO_2 and HCl are also related to ozone concentration. Grooß et al. (1997) showed that HCl increases more rapidly in the Antarctic polar vortex than in the Arctic polar vortex due to lower ozone concentrations in the Antarctic polar vortex. Low ozone reduces the rate of reaction (R8), and then Cl/ClO ratio becomes high. Low ozone also reduces the rate of the following reaction:



This makes NO/NO_2 ratio high and increases Cl/ClO ratio by the following reaction:



High Cl/ClO ratio leads to rapid HCl formation by reactions (R13) and (R14), and reduces the formation ratio of ClONO_2 by reaction (R12) (Grooß et al., 2011; Müller et al., 2018).

The processes of deactivation of active chlorine are different between typical conditions in the Antarctic and those in the Arctic. In the Antarctic, the temperature cools below the NAT PSC formation threshold (about 195 K at 50 hPa) in the whole area of the polar vortex in almost years, and almost complete denitrification and chlorine activation occur (WMO, 2007), followed by severe ozone depletion in spring. In the chlorine reservoir recovery phase, HCl is mainly formed by reaction (R13) due to the lack of ozone (typically less than 0.5 ppmv) by the mechanism described in the previous paragraph (Grooß et al., 2011).

On the other hand, in the Arctic, typically less PSC formation occurs in the polar vortex due to generally higher stratospheric temperatures (~10-15K in average) compared with that of Antarctica. Then only partial denitrification and chlorine activation occur in some years (Manney et al., 2011; WMO, 2014). In this case, some ozone and NO_2 are available in the chlorine reservoir recovery phase. Therefore, the ClONO_2 amount becomes sometimes higher than that of HCl after PSCs have disappeared due to the rapid reaction (R12) (Michelsen et al., 1999; Santee et al., 2003), which results in additional increase of ClONO_2 than pre-winter value at the time of chlorine deactivation in spring (von Clarmann et al., 1993; Müller et al., 1994; Oelhaf et al., 1994). In this way, the partitioning of chlorine reservoir in springtime is related to temperature, PSC amounts, ozone, and NO_2 concentrations (Santee et al., 2008; Solomon et al., 2015).

In the polar regions, the ozone and related atmospheric trace gas species have been intensively monitored by several measurement techniques since the discovery of the ozone hole. These measurements consist of direct observations by high-altitude aircrafts (e.g., Anderson et al., 1989; Ko et al., 1989; Tuck et al., 1995; Jaeglé et al., 1997; Bonne et al., 2000), remote sensing observations by satellites (e.g., Müller et al., 1996; Michelsen et al., 1999; Höpfner et al., 2004; Dufour et al., 2006; Hayashida et al., 2007), remote sensing observations of OCIO using UV-visible spectrometer from the ground (Solomon et al., 1987; Kreher et al., 1996), remote sensing observations of ClO by microwave spectrometer from ground (de Zafra et al., 1989), (e.g., Farmer et al., 1987; Kreher et al., 1996; Solomon et al., 1997; Mellqvist et al., 2002; Blumenstock et al., 2006). Within these observations, ground-based measurements have the characteristic of high temporal resolution. In addition, the Fourier-Transform infrared spectrometer (FTIR) has the capability of measuring several trace gas species at the same time or in a short time interval (Rinsland et al., 1988). In this paper, we show the results of ground-based FTIR observations of O₃ and other trace gas species at Syowa Station in the Antarctic in 2007 and 2011, combined with the satellite measurements of trace gas species by Microwave Limb Sounder onboard the Aura satellite (Aura/MLS) and Michelson Interferometer for Passive Atmospheric Sounding onboard the European Environmental Satellite (Envisat/MIPAS), to show the temporal variation and partitioning of active chlorine (ClO_x) and chlorine reservoirs (HCl, ClONO₂) from fall to spring during the ozone hole formation and dissipation period. In order to monitor the appearance of PSCs over Syowa Station, we used the Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) data onboard the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) satellite. The methods of FTIR and satellite measurements are described in Section 2. The validation of FTIR measurements is described in Section 3. The results of FTIR and satellite measurements and discussion on the behavior of active and inert chlorine species using the MIROC3.2 chemistry-climate model are described in Section 4.

2. Measurements

2.1 FTIR measurements

The Japanese Antarctic Syowa Station (69.0°S, 39.6°E) was established in January 1957. Since then, several scientific observations related to meteorology, upper atmospheric physics, glaciology, biology, geology, seismology, etc. have been performed. The ozone hole was first detected by Dobson spectrometer and ozonesonde measurements from Syowa Station in 1982 (Chubachi, 1984) and by Dobson spectrometer measurement at Halley Bay (Farman et al., 1985). We installed a Bruker IFS-120M high-resolution Fourier-Transform infrared spectrometer (FTIR) in the Observation Hut at Syowa Station in March 2007. This was the ~~third~~^{second} high-resolution FTIR site in Antarctica in operation after U.S.A.'s South Pole Station (90.0°S) (Goldman et al., 1983; Goldman et al., 1987; Murcray et al., 1987), U.S.A.'s McMurdo Station and New Zealand's Arrival Heights facility at Scott Station (77.8°S, 166.7°E) (Farmer et al., 1987; Murcray et al., 1989; Kreher et al., 1996; Wood et al., 2002; Wood et al., 2004). The IFS-120M FTIR has a wavenumber resolution of 0.0035 cm⁻¹, with two liquid nitrogen cooled detectors (InSb and HgCdTe covering the frequency ranges 2000-5000 and 700-1300 cm⁻¹, respectively) with six optical filters.

and fed by an external solar tracking system. One measurement takes about 10 minutes. At least, six spectra were taken per day covering each filter region. Since Syowa Station is located at a relatively low latitude (69.0°S) compared with McMurdo or Scott Stations (77.8°S), there is an advantage of the short (about one month) polar night period, when we cannot measure atmospheric species using the sun as a light source. Since FTIR measurements at Syowa Station are possible from early spring (late July), FTIR can measure chemical species during ozone hole development. On the other hand, FTIR observations become possible only after September at McMurdo and Scott Stations. Another advantage of Syowa Station is that itthe locatesion at vortex boundary as well as inside and outside of the polar vortex and this enables us to measure chemical species at the both inside and outside of the polar vortex, different regions of polar chemistry related to ozone hole, since the station is sometimes located near the edge of the polar vortex. From March to December 2007, we made in total 78 days of FTIR measurements on sunny days. Another 19 days of FTIR measurements were performed from September to November 2011. After a few more measurements were performed in 2016, the FTIR was brought back to Japan in 2017. In Appendix, Table A1 shows the days when FTIR measurements were made at Syowa Station with the information inside/boundary/outside of the polar vortex defined by the method described in Appendix A2Section 4 using ERA-Interim reanalysis data. Strahan et al. (2014) showed the year-to-year variation of Cl_y observed in the lower stratosphere of the Antarctic polar vortex. The Cl_y observed in 2007 (2.88 ppbv) was about +4.3% more and that observed in 2011 (2.53 ppbv) was about -5.2% less than the projected Cl_y from Newman et al. (2007) (2.76 ppbv for 2007 and 2.67 ppbv for 2011).

The retrieval of the FTIR spectra was done with SFIT2 Version 3.92 program (Rinsland et al., 1998; Hase et al., 2004). SFIT2 retrieves a vertical profile of trace gases using an optimal estimation formulation of Rodgers (2000), implemented with a semi-empirical method which was originally developed for microwave measurements (Parrish et al., 1992; Connor et al., 1995). The SFIT2 forward model fully describes the FTIR instrument response, with absorption coefficients calculated using the algorithm of Norton and Rinsland (1991). The atmosphere is constructed with 47 layers from the ground to 100 km, using the FSCATM (Gallery et al., 1983) program for atmospheric ray-tracing to account for refractive bending. The retrieval parameters for each gas, typical vertical resolution, and typical degrees of freedoms (DOFS) are shown in Table 12. Temperature and pressure profiles between 0 and 30 km are taken by the Rawin sonde observations flown from Syowa Station on the same day by the Japanese Meteorological Agency (JMA), while values between 30 and 100 km are taken from the COSPAR International Reference Atmosphere 1986 (CIRA-86) standard atmosphere profile (Rees et al., 1990).

We retrieved vertical profiles of O_3 , HCl , and HNO_3 from the solar spectra. We used monthly averaged ozonesondes profiles (0-30 km) and Improve Limb Atmospheric Spectrometer-II (ILAS-II) (Nakajima, 2006; Nakajima et al., 2006; Sugita et al., 2006) profiles (30-100 km) for the a priori of O_3 , monthly averaged profiles from ILAS-II for HNO_3 and monthly averaged profiles from HALOE (Anderson et al., 2000) for HCl . We focus on the altitude range of 15-25 km in this study. Typical averaging kernels of the SFIT2 retrievals for O_3 , HNO_3 , and HCl are shown in Figures 1(a), (b), and (c), respectively.

2.2 Satellite measurements

The Earth Observing System (EOS) MLS onboard the Aura satellite was launched on 15 July 2004, to monitor several atmospheric chemical species in upper troposphere to mesosphere (Waters et al., 2006). The Aura orbit is sun-synchronous at 705 km altitude with an inclination of 98°, 13:45 ascending (north-going) equator-crossing time, and 98.8-min period. Vertical profiles are measured every ~165 km along the suborbital track, horizontal resolution is ~200-600 km along-track, ~3-10 km across-track, and vertical resolution is ~3-4 km in the lower to middle stratosphere (Froidevaux et al., 2006). ClO, HCl, and HNO₃ profiles used in this study were taken from Aura/MLS version 4.2 data (Liversey et al., 2006; Santee et al., 2011; Ziemke et al., 2011; Liversey et al., 2018). Only daytime ClO data was used for the analysis. The MLS data were taken from the following site: <http://avdc.gsfc.nasa.gov/index.php?site=2045907950>. The daily MLS data within 320 km distance between was selected whose the measurement location and is within 300 km radius from Syowa Station and within ±6 hours of the FTIR measurement were selected.

MIPAS is a Fourier transform spectrometer sounding the thermal emission of the earth's atmosphere between 685 and 2410 cm⁻¹ (14.6-4.15 μm) in limb geometry (Fischer and Oelhaf, 1996; Fischer et al., 2008). The maximum optical path difference of MIPAS is 20 cm. The field-of-view of the instrument at the tangent points is about 3 km in the vertical and 30 km in the horizontal. In the standard observation mode in one limb-scan, 17 tangent points are observed with nominal altitudes 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 39, 42, 47, 52, 60, and 68 km. In this mode, about 73 limb scans are recorded per orbit. The measurements of each orbit cover nearly the complete latitude range from about 87°S to 89°N. MIPAS was put on board the Envisat, which was launched on 1 March 2002, and was put into a polar sun-synchronous orbit at an altitude of about 800 km with an inclination of 98.55° (von Clarmann et al., 2003). On its descending node, the satellite crosses the equator at 10:00 local time. Envisat performs 14.3 orbits per day, which results in a good global coverage. ClONO₂ profiles which we used in this study were taken from Envisat/MIPAS IMK/IAA version V5R_CLONO2_220 and V5R_CLONO2_222 (Höpfner et al., 2007). The MIPAS data were taken from the following site: http://share.lsd.fkit.edu/imk/asf/sat/mipas-export/Data_by_Target/. The selection criteria of the daily MIPAS data within 320 km distance between the measurement location and Syowa Station used in this study are the same as that of Aura/MLS were selected.

The CALIPSO satellite was launched on 28 April 2006. On CALIPSO satellite, CALIOP instrument was on board, to monitor aerosols, clouds, and PSCs (Pitts et al., 2007). CALIOP is a two-wavelength, polarization sensitive lidar that provides high vertical resolution profiles of backscatter coefficient at 532 and 1064 nm, as well as two orthogonal (parallel and perpendicular) polarization components at 532 nm (Winker et al., 2007). The CALIOP data were taken from the following site: https://www-calipso.larc.nasa.gov/resources/calipso_users_guide/data_summaries/psc/index.php. In order to monitor the appearance of PSCs over Syowa Station, we used the daily CALIOP PSC data (Pitts et al., 2007; 2009; 2011) within 320 km distance between the measurement location and Syowa Station were selected.

3. Validation of retrieved profiles from FTIR spectra with other measurements

We validated retrieved FTIR profiles of O₃ with ozonesondes, ~~and HNO₃ and HCl with~~ and Aura/MLS version 3.3 data (Livesey et al., 2013) for 2007 measurements. ~~Also, retrieved FTIR profiles of HNO₃ and HCl were validated with Aura/MLS data.~~ We identified the nearest Aura/MLS data from the distance between the Aura/MLS tangent point at 20 km altitude and the point at 20 km altitude for the direction of the sun from Syowa Station at the time of the FTIR measurement. The spatial and temporal collocation criteria used was within 300 km radius and ±6 hours, ~~as stated in Section 2.2.~~ The ozonesonde and Aura/MLS profiles were interpolated onto a 1 km-grid, then smoothed ~~using with~~ a 5 km-wide ~~running means~~ slit function.

Figures 2(a)-(b) show absolute and relative ~~percentage~~ differences of O₃ profiles retrieved from FTIR measurements and those from model 1Z ECC-type ozonesonde measurements, respectively, calculated from 14 coincident measurements from September 5 to December 17, 2007. Typical precision and accuracy of the ECC-type ozone sondes are considered to be ±(3-5)% and ±(4-5)%, respectively (Komhyr, 1986). We define the relative percentage difference D as:

$$D (\%) = 100 * (FTIR-sonde) / ((FTIR+sonde)/2). \quad (1)$$

The mean absolute difference between 15 and 25 km was within -0.02 to 0.40 ppmv. The mean relative difference D between 15 and 25 km was within -10.4 to +24.4%. The average of mean relative differences D of O₃ for the altitude of interest in this study (18-22 km) was +6.1%, with the minimum of -10.4% and the maximum of +19.2%. FTIR data agree with validation data within root mean squares of typical errors in FTIR and validation data ~~error bars~~ at the altitude of interest. Note that relatively large D values between 16 and 18 km are due to small ozone amount in the ozone hole. Our validation results are quite comparable with other validation study at Izaña Observatory by Schneider et al. (2008).

Figures 2(c)-(d) show absolute and relative differences of O₃ profiles retrieved from FTIR measurements and those from Aura/MLS measurements, respectively, calculated from 33 coincident measurements from April 1 to December 20, 2007. The accuracy of MLS O₃ data are reported to be 5-8% between 0.5 and 46 hPa (Livesey et al., 2013). The mean absolute difference ~~agreement~~ between 15 and 25 km was within -0.13 to +0.16 ppmv. The mean relative difference D between 15 and 25 km was within -16.2 to +5.2%. The average of mean relative differences D for O₃ for the altitude of interest in this study (18-22 km) was -5.5%, with the minimum of -16.3% and the maximum of +4.5%. Froidevoux et al. (2008) showed that Aura/MLS is +8% higher than ACE-FTS at 70°S, which may explain the negative bias of FTIR data compared with MLS data.

Figures 2(e)-(f) show absolute and ~~relative~~ percentage differences of HNO₃ profiles retrieved by FTIR measurements and those from Aura/MLS measurements, respectively, calculated from 47 coincident measurements from March 25 to December 20, 2007. The mean absolute difference ~~agreement~~ between 15 and 25 km was within -0.56 to +0.57 ppbv. The mean relative difference D between 15 and 25 km was within -25.5 to +21.9%. The average of mean relative differences D for HNO₃ for the altitude of interest in this study (18-22 km) was +13.2%, with the minimum of +0.2% and the maximum of +21.9%. This positive bias of FTIR data is still within the error bars of FTIR measurements. Livesey et al. (2013) showed that Aura/MLS version 3.3 data has no bias within errors (~0.6-0.7 ppbv (10-12%) at pressure level of 100-3.2 hPa) compared with other

measurements. [Livesey et al. \(2018\)](#) showed no major differences between Aura/MLS version 3.3 and version 4.2 data for HNO_3 .

Figures 2(g)-(h) show absolute and relative ~~percentage~~ differences of HCl profiles retrieved by FTIR measurements and those from Aura/MLS measurements, respectively, calculated from 50 coincident measurements from March 25 to December 20, 2007. The ~~mean absolute difference~~ agreement between 15 and 25 km was within -0.20 to -0.09 ppbv. The ~~mean~~ relative difference D between 15 and 25 km was within -34.1 to -3.0%. The ~~average of~~ mean relative differences D for HCl for the altitude of interest in this study (18-22 km) is -9.7%, with a minimum of -14.6% and a maximum of -3.0%. This negative bias of FTIR data is still within the error bars of FTIR measurements. Moreover, Livesey et al. (2013) showed that Aura/MLS version 3.3 values are systematically greater than HALOE values by 10-15% with a precision of 0.2-0.6 ~~ppbv%~~ (10-30%) in the stratosphere, which may partly explain the negative bias of FTIR data compared with MLS data. [Livesey et al. \(2018\)](#) showed no major differences between Aura/MLS version 3.3 and version 4.2 data for HCl.

Table 23 summarizes validation results of FTIR profiles compared with ozonesonde or Aura/MLS measurements, and possible Aura/MLS biases from literature.

4. Results and discussion

4.1 Time series of observed species

Figures 3(a) ~~shows daytime hours at Syowa Station. Polar night ends at Syowa Station on July 14 (day 195).~~ Figures 3(b)-(c) show the time series of temperatures at 18 and 22 km over Syowa Station using ERA-Interim data (Dee et al., 2011) for 2007 and 2011. Approximate saturation temperatures for NAT PSC (T_{NAT}) and ice PSC (T_{ICE}) calculated by assuming 6 ppbv HNO_3 and 4.5 ppmv H_2O are also shown in the figures. The dates when PSCs were observed at Syowa Station identified by the nearest CALIOP data of that day were indicated by asterisks ~~at~~ on the bottom of the figures. Over Syowa Station, PSCs ~~were observed when temperature fell ~4K below T_{NAT} .~~ PSCs were often observed at 15-25 km from the beginning of July (day 183) to ~~late August~~ the middle of September (day 241-53) in 2007, and from late June (day 175) to early September (day 251) in 2011.

PSCs were observed only at 18 km after August, due to the sedimentation of PSCs and downwelling of vortex air in late winter as is seen in Figure 3. Although temperatures above Syowa Station were sometimes below T_{NAT} in June and in late September, no PSC was observed during those periods. This may be due to other reasons, such as a different time history of temperature for PSC formation, and/or low HNO_3 (denitrification) and/or H_2O concentration (dehydration) which are needed for PSC formation in late winter season (Saitoh et al., 2006).

Figures 4-7 show time series of HCl, ClONO_2 , ClO, Cl_y^* , O_3 , and HNO_3 over Syowa Station in 2007 and 2011 at altitudes of 18 and 22 km for all ground-based and satellite-based observations used in this study, respectively. O_3 (sonde) is observed with the KC96 ozonesonde for 2007, ~~which is different from the ones that were used for the validation in Section 3,~~ and the

ECC-1Z ozonesonde for 2011 by JMA (Smit and Straeter, 2004). HCl and HNO₃ observed by Aura/MLS and FTIR are plotted by different symbols to complement the data lack of FTIR measurements. ClONO₂ observed by Envisat/MIPAS is also plotted in the figure. Total inorganic chlorine Cl_y* corresponds to the sum of HCl, ClONO₂, and Cl_x, where active chlorine species Cl_x is defined as the sum of ClO, Cl, and 2*Cl₂O₂ (Bonne et al., 2000). It is known that total inorganic chlorine Cl_y* has compact relation with N₂O (Bonne et al., 2000; Schauffler et al., 2003; Strahan et al., 2014). Inferred total inorganic chlorine Cl_y* is calculated from N₂O value (in ppbv) measured by MLS and by using the empirical polynomial equation derived from the correlation analysis of Cl_y and N₂O from the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission which took place from April to September 1997 (Bonne et al., 2000):

$$\text{Cl}_y^*(\text{pptv}) = 4.7070 \times 10^{-7} (\text{N}_2\text{O})^4 - 3.2708 \times 10^{-4} (\text{N}_2\text{O})^3 + 4.0818 \times 10^{-2} (\text{N}_2\text{O})^2 - 4.6856 (\text{N}_2\text{O}) + 3225. \quad (2)$$

If we consider the change of the Cl_y, the estimated Cl_y* in 2007 might be -0.7% less than this value, while that in 2011 might be -12.8% less than this value (Strahan et al., 2014).

A transport barrier of minor constituents at the edge of polar vortex was reported by Lee et al. (2001) and Tilmes et al. (2006). The distribution of minor constituents is quite different among inside, the boundary region, and outside the polar vortex. The dark shaded area, the light shaded area, and the white area indicate the days when Syowa Station was located outside, in the boundary region, and inside the polar vortex, respectively. In Antarctic winter, there are often double peaks in isentropic potential vorticity gradient with respect to equivalent latitude at 450-600 K level (Tomikawa et al., 2015). The method to determine the three polar regions, i.e., inside the polar vortex, the boundary region, and outside the polar vortex is described in Appendix B. Inner and outer edges of the polar vortex were determined as follows:

1) Equivalent latitudes (McIntyre and Palmer, 1984; Butchart and Remsberg, 1986) were computed based on isentropic potential vorticity at 450 K and 560 K isentropic surfaces for 18 km and 22 km using the ERA-Interim reanalysis data (Dee et al., 2011), respectively.

2) Inner and outer edges (at least 5° apart from each other) of the polar vortex were defined by local maxima of the isentropic potential vorticity gradient with respect to equivalent latitude only when a tangential wind speed (i.e., mean horizontal wind speed along the isentropic potential vorticity contour; see Eq. (1) of Tomikawa and Sato (2003)) near the vortex edge exceeds a threshold value (i.e., 20 m s⁻¹; see Nash et al. (1996) and Tomikawa et al. (2015)).

3) Then, the polar region is divided into three regions; i.e., inside the polar vortex (inside of inner edge), the boundary region (between inner and outer edges), and outside the polar vortex (outside of outer edge).

Note that the Syowa Station is often located near the vortex edge and the temporal variations of chemical species observed over Syowa Station reflect the spatial distributions as well as local chemical evolution. When Syowa Station was located at the boundary region or outside the polar vortex (e.g., day 310-316 in Figure 4, day 192-195 in Figure 5, day 309-316 in Figure 6, day 276-282 in Figure 7), chemical species showed different values compared with the ones inside the polar vortex. The lack of data for ClO and HCl (MLS) from day 195 to day 219, 2007 and ClONO₂ from day 170 to day 216, 2007 (upper panels of Figures 4(a) and 6(a)) is due to unrealistic large error values in Aura/MLS or Envisat/MIPAS data products measurements during this period.

The altitude of 18 km was selected because it was one of the altitudes where nearly complete ozone loss was occurred. The altitude of 22 km, where only about half of the ozone was depleted, was selected to show the difference in the behavior of chemical species from that at 18 km.

The general features of the chemical species observed inside the polar vortex at 18 and 22 km in 2007 and 2011 are summarized as follows: HCl and ClONO₂ decreased first, then ClO started to increase in winter, while HCl increases and ClO decreases were synchronized in spring. HCl was almost zero from late June to early September and the day-to-day variations were small over this period. (HCl over Syowa Station indicates relatively larger values when it was located ~~at the polar vortex boundary or~~ outside the polar vortex: For example, early August and the beginning of September at 22 km, 2007 in Figure 6). HNO₃ showed large decreases from June to July, and then gradually increased in summer. Day-to-day variations of HNO₃ from June to August were large. O₃ decreased from July to late September when ClO concentration was increased. ClO was enhanced in August and September and the day-to-day variations were large over this period. Cl_y* gradually increased in the polar vortex from late autumn to spring. The Cl_y* value became larger compared with its mixing ratio outside of the polar vortex in spring.

The following characteristics are evident at 18 km (Figures 4 and 5). O₃ gradually decreased from values of 2.5-3 ppmv before winter to values less than one fifth, 0.3-0.5 ppmv, in October. The values of HCl from late June to early September were as small as 0-0.3 ppbv. The recovered values of HCl inside the vortex in spring (October-December) were larger than those before winter and those outside the polar vortex during the same period. ClONO₂ inside the vortex kept near zero even after ClO disappeared and did not recover to the level before winter until spring.

At 22 km (Figures 6 and 7), O₃ gradually decreased from winter to spring, but the magnitude of the decrease was much smaller than that at 18 km. The values of HCl from late June to early September were 0-1 ppbv, larger than those at 18 km. The recovered values of HCl in spring were nearly the same as those before winter (around 2.2 ppbv). ClONO₂ recovered to larger values than those before winter after ClO disappeared.

As for the temporal increase of ClONO₂ in spring during the ClO decreasing phase, we can see a peak of 1.5 ppbv at 18 km in 2011, and at 22 km in both 2007 and 2011 around September 27 (day 270), but we see no temporal increase of ClONO₂ at 18 km in 2007.

Figure 7 shows that temporal ClO enhancement and decrease of O₃, ClONO₂, and HNO₃ occurred in early winter (May 30-June 19; day 150-170) at 22 km in 2011. This small ozone depletion event before winter may be due to an air mass movement from the polar night area to a sunlit area at lower latitudes. ~~Table 4 summarized the characteristics of variation of minor atmospheric species for 2007 and 2011 at altitudes of 18 and 22 km.~~

4.2 Time series of ratios of chlorine species

In order to discuss the temporal variations of the chlorine partitioning, the ratios of observed HCl, ClONO₂, and ClO, ~~and~~ Cl_y with respect to Cl_y* were calculated. Hereafter, we will discuss the ratios of chlorine species only for the cases when Syowa Station was located inside the polar vortex. ~~Here, observed Cl_y is determined as:~~

$$-\text{Cl}_y(\text{FTIR}) = \text{HCl}(\text{FTIR}) + \text{ClONO}_2(\text{MIPAS}) + \text{ClO}(\text{MLS}) \quad (3)$$

$$\text{Cl}_y(\text{MLS}) = \text{HCl}(\text{MLS}) + \text{ClONO}_2(\text{MIPAS}) + \text{ClO}(\text{MLS}). \quad (4)$$

Figures 8 and 9 show the time series of the ratios of each chlorine species with respect to Cl_y^* in 2007 (a) and in 2011 (b) at 18 km and 22 km, respectively. In these plots, HCl data by Aura/MLS were used. Note that light blue in these figures

shows either ClONO_2 or ClO data was missing on that day, while dark blue shows all three data were available on that day.

For both in 2007 and 2011 at 18 km (Figure 8), the ratio of HCl was 0.6-0.8 and the ratio of ClONO_2 was 0.2-0.3 before winter (May 10-20; day 130-140). The ratio partitioning of HCl to Cl_y^* was three times larger than that of ClONO_2 at that time. The ratio of ClO increased to ~ 0.5 - 0.6 during the ClO enhanced period (the period when ClO values were more than 80 % of its maximum value: August 18-September 17; day 230-260. See Table 4). The ratio of HCl was 0-0.2 and the ratio of ClONO_2 was 0-0.6 during this same period. ClONO_2 shows negative correlation with ClO, while HCl kept low even when ClO was low during this period. This negative correlation is shown in Figure 10 later. When ClO was enhanced, the O_3 amount gradually decreased, and finally reached <0.5 ppmv ($>80\%$ destruction) in October (October 7; day 280) (See Figures 4 and 5). The ratios became 0.9-1.0 for HCl and 0-0.1 for ClONO_2 after the recovery in spring (after October 17; day 290), indicating that almost all chlorine reservoir species became HCl via reactions (R13) and/or (R14), due to the lack of O_3 and NO_2 during this period. The sum ratios of $\text{HCl} + \text{ClONO}_2 + \text{ClO}$ $\text{Cl}_y(\text{FTIR})$ and $\text{Cl}_y(\text{MLS})$ were both around 0.5 - 0.8 - 0.7 at the time of ClO enhanced period (August 18-September 17; day 230-260). The remaining chlorine is thought to be either Cl_2O_2 or HOCl , which will be shown in model simulation result in Section 4.6. The sum ratio of $\text{HCl} + \text{ClONO}_2$ Cl_y became close to 1 after the recovery period (after October 7; day 280).

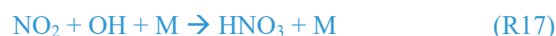
For both in 2007 and 2011 at 22 km (Figure 9), the ratio of HCl was 0.8 - 0.9 and the ratio of ClONO_2 was 0.2-0.3 before winter (April 20-May 20; day 110-140). The ratio partitioning of HCl was three to four times larger than that of ClONO_2 . The ratio of ClO increased to 0.5 - 0.7 during the ClO enhanced period (August 8-28; day 220-240 in 2007, August 18-September 7; day 230-250 in 2011). The ratio of HCl was 0-0. 23 and the ratio of ClONO_2 was 0-0.6 during this period. ClONO_2 shows negative correlation with ClO, while HCl kept low even when ClO was low during this period as in the case at 18 km. The O_3 amount gradually decreased during the ClO enhanced period but kept the concentration more than 1.5 ppmv (less than half destruction) at this altitude (See Figures 6 and 7). When the ClO enhancement ended, temporal increase of both ClONO_2 and HCl occurred simultaneously up to a ratio of 0.5 occurred in early spring (September 17-October 7; day 260-280). Then, the reservoir ratios became 0.6-0. 78 for HCl and 0. 32 -0.4 for ClONO_2 in spring (after October 7; after day 280). This phenomenon shows that more chlorine deactivation via reaction (R12) occurred towards ClONO_2 at 22 km rather than at 18 km. This is attributed to the existence of O_3 and NO_2 during this period at 22 km, which was different from the case at 18 km. The sum ratios of $\text{HCl} + \text{ClONO}_2 + \text{ClO}$ $\text{Cl}_y(\text{FTIR})$ and $\text{Cl}_y(\text{MLS})$ were both around 0.7 - 1.0 - 0.8 at the time of ClO enhanced period (August 8-28; day 220-240 in 2007, August 18-September 7; day 230-250 in 2011). The remaining chlorine is thought to be either Cl_2O_2 or HOCl . The sum ratio of $\text{HCl} + \text{ClONO}_2 + \text{ClO}$ Cl_y became around 1.1 after the recovery period (after September 27; day 270). The reason why observed sum ratio Cl_y values exceed calculated Cl_y^* values might be because the $\text{N}_2\text{O}-\text{Cl}_y$ correlation from the one in the equation (2) is not applicable at this altitude.

In 2011 at 18 km (Figure 8), another temporal increase of ClONO₂ up to a ratio of 0.46 occurred in early spring (around October 2-127; day 275-2859) in accordance with HCl increase, then the ClONO₂ amount gradually decreased to nearly zero after late October (after October 27; day 300). This temporal increase in ClONO₂ could be attributed to temporal change of the location of Syowa Station in the polar vortex. Although Syowa Station was judged to be inside the polar vortex during July 14-December 16 (day 195-350) by our analysis, the difference between the equivalent latitude over Syowa Station and that at inner edge became less than 10 degrees at around October 7 (day 280), while it was typically between 15 and 20 degrees in other days. O₃ and HNO₃ showed higher values around October 7 (day 280) (see Figure 5), indicating that Syowa Station was located close to the boundary region at this period (See Figure A2). Therefore, the temporal increase of ClONO₂ in 2011 at 18 km was attributed to spatial variation, not to chemical evolution.

4.3 Correlation between ClO and ClONO₂

Figure 10 shows the correlation between ClO and ClONO₂ during the ClO enhanced period (August 8-September 17; day 220-260) at 18 km in 2007 (a) and 2011 (b), and at 22 km in 2007 (c) and 2011 (d). In this plot, the location of Syowa Station with respect to the polar vortex (inside, the boundary region, and outside the polar vortex) is indicated by different symbols. Note that MLS ClO and MIPAS ClONO₂ data were sampled on the same day at the nearest orbit to Syowa Station for both satellites. The maximum differences between these two satellites' observational times and locations are 9.0 hours in time and 587 km in distance. Mean differences are 6.8 hours in time and 270 km in distance, respectively. Solid lines show regression lines obtained by RMA (Reduced Major Axis (RMA) regression. Negative correlations of slope about -1.0 between ClO and ClONO₂ are seen in all figures.

The negative correlation between ClO and ClONO₂ at Syowa Station is explained by the difference in the concentration of ClO, NO₂, ClONO₂, and HNO₃ inside, outside, and at the boundary region of the polar vortex around the station. Outside of the polar vortex, ClO concentration is lower and NO₂ concentration is higher than those inside the polar vortex. Inside of the polar vortex, HNO₃ is taken into PSCs and removed by the sedimentation of PSCs from the lower stratosphere (denitrification process). Then NO_x concentration is low because HNO₃ is a reservoir of NO_x through the reactions:



and



Then NO₂ concentration is low and ClONO₂ concentration is also low due to the consumption of ClONO₂ by heterogeneous reaction (R2) inside the polar vortex. In spring, ClO amount gets high due to the activation of chlorine species by reactions (R1~R8) inside the polar vortex. At the boundary region, ClO and NO₂ concentrations indicate the value between inside and outside of the polar vortex, that is, ClO concentration is much higher than that outside of the polar vortex and NO₂ concentration is much higher than that inside of the polar vortex. Thus, ClONO₂ concentration there is elevated in August-September due to the reaction (R12). This cause the ~~The cause of this~~ negative correlation between ClO and ClONO₂ might be ~~due to the variation of the~~ relative distance between Syowa Station and the boundary region ~~edge~~ of the polar vortex. When Syowa

Station was located deep inside the polar vortex, there was more ClO and less ClONO₂. On the contrary when Syowa Station was located near the vortex edge, there was less ClO and more ClONO₂. The equivalent latitude (EL) over Syowa Station was calculated as described in Appendix B for each correlation point. The EL in each correlation point is now shown by the color code in Figure 10. It generally shows the tendency, that warm coloured higher equivalent latitude points are located more towards the bottom right-hand side. This is further confirmed by 3-dimensional model simulation as shown later.

4.4 Comparison with model results

Figures 11 and 12 show comparisons of daily time series of simulated mixing ratios of ClO, HCl, ClONO₂, Cl_y, and O₃ by the MIROC3.2 Chemistry-Climate Model (CCM) (Akiyoshi et al., 2016) with FTIR, Aura/MLS, and Envisat/MIPAS measurements at 18 km and 22 km, respectively. For a description of the MIROC3.2 CCM, please see Appendix A for detail. In these figures, Cl_y for Aura/MLS in the panels (d) and (i) actually represents the Cl_y* value calculated by equation (2) using the N₂O value measured by Aura/MLS. Cl_y from the MIROC3.2 CCM is the sum of total reactive chlorines, i.e., Cl_y = Cl + 2*Cl₂ + ClO + 2*Cl₂O₂ + OCIO + HCl + HOCl + ClONO₂ + ClNO₂ + BrCl. Note that we plotted modeled values at 12h UTC (~15h local time of Syowa Station) calculated by the MIROC3.2 CCM in order to compare the daytime measurements of FTIR and satellites. In Figures 11(b), (d), (g), and (i), modeled HCl and Cl_y showed systematically smaller by 20-40% values compared with FTIR or MLS measurements. The cause of this discrepancy may be partly due to either smaller downward advection and/or faster horizontal mixing of air mass across the subtropical barrier in MIROC3.2 CCM (Akiyoshi et al., 2016). Another possibility of the discrepancy is the difference of Cl_y*-N₂O correlation used to calculate the Cl_y* value by equation (2), since this correlation comes from the aircraft measurement in summer in 1997 (Bonne et al., 2000), and our observations are in winter in 2007 and 2011, when projected Cl_y was -0.7% and -12.8% smaller than in 1997, respectively (Strahan et al., 2014). Nevertheless, evolutions of measured HClO and ClONO₂ for the period are well simulated by the MIROC3.2 CCM. Modeled O₃ were in very good agreement with FTIR and/or MLS measurements throughout the year in both altitudes for both years. Hereafter, the result of MIROC3.2 CCM at 50 hPa (~18 km) is discussed.

4.5 Polar distribution of minor species

Figure 13 shows distributions of temperature from the model nudged toward the ERA-Interim data, simulated mixing ratios of O₃, NO₂, HNO₃, ClO, HCl, and ClONO₂ by the MIROC3.2 CCM at 50 hPa for June 24 (day 175), September 2 (day 245), September 6 (day 249), and October 6 (day 279) in 2007. Polar vortex edges boundary defined by the method described in Appendix B maximum gradient of potential vorticity at 475 K calculated from ERA-Interim reanalysis data were as plotted by white dotted circles. This boundary was located in between the inner and the outer edges of the polar vortex as were defined in Section 4.1. The location of Syowa Station is shown by a white star in each panel. On June 24 (day 175), stratospheric temperatures over Antarctica were already low enough for the onset of heterogeneous chemistry to allow PSCs to form. Consequently, NO₂ was converted into HNO₃ via reaction (R17), and HNO₃ in the polar vortex was condensed onto PSCs. Note that the depleted area of NO₂ was greater than that of HNO₃. This is due to the occurrence of reaction (R12) that converts

CIO and NO₂ ~~into~~ ClONO₂ at the edge of the polar vortex, which is shown by the enhanced ClONO₂ area at the vortex edge in Figure 13. Also, HCl and ClONO₂ are depleted in the polar vortex due to the heterogeneous reactions (R1), (R2), (R3), and (R4) on the surface of PSCs and aerosols. Some HCl remains near the core of the polar vortex, because the initial amount of the counter-part of heterogeneous reaction (R1) (ClONO₂) was less than that of HCl, as was also shown by CLaMS model simulation by Grooß et al. (2018). The O₃ amount was only slightly depleted within the polar vortex on this day.

On September 2 (day 245), amounts of NO₂, HNO₃, HCl, and ClONO₂ all show very depleted values in the polar vortex. The amount of ClO shows some enhanced values ~~at the outer part inside of~~ the polar vortex. Development of ozone depletion was seen in the polar vortex. Note that ClONO₂ shows enhanced values around the boundary region of the polar vortex. This might be due to the reaction (R12) at this location. On this day (day 245), Syowa Station was located inside the polar vortex close to the ~~inner~~-vortex edge, where ClO was smaller and ClONO₂ was greater than the values deep inside the polar vortex as observed and indicated by upper left circle with cross in Figure 10 (a).

On September 6 (day 249), most features were the same as on September 2, but the shape of the polar vortex was different. Consequently, Syowa Station was located deep inside the polar vortex, where ClO was greater and ClONO₂ was smaller than the values around the boundary region of the polar vortex as observed and indicated by lower right circle with cross in Figure 10 (a). Hence, the negative correlation between ClO and ClONO₂ seen in Figure 10 was due to variation of the relative distance between Syowa Station and the ~~inner~~-edge of the polar vortex.

As for HCl, it kept nearly zero value not only on this day (September 6) but also on September 2 when Syowa Station was located inside the polar vortex close to the ~~inner~~-vortex edge. Therefore, observed day-to-day variations of HCl were small and did not show any correlation with ClO (see Figures 4-7). A possible explanation to keep near zero HCl low value near the vortex edge is due to a so-called “HCl-null cycles” which was started with fast reaction (R13) proposed by Müller et al. (2018). This cycle is discussed later.

On October 6 (day 279), ClO enhancement has almost disappeared. Inside the polar vortex, O₃, NO₂, HNO₃, and ClONO₂ showed very low values. Ozone was almost fully destroyed at this altitude in the polar vortex. However, the amount of HCl increased deep inside the polar vortex. This might be due to the recovery of HCl by reactions (R13) and/or (R14) deep inside the polar vortex, where there was no O₃ or NO₂ left and reactions (R13) and/or (R14) ~~were~~ favoured compared with reaction (R12). Syowa Station was located deep inside the polar vortex and the simulated and observed amounts of HCl were both more than ten times greater than those of ClONO₂ on this day (see Figure 4).

Figure 14 shows ~~the distributions~~ of temperature from the model nudged toward the ERA-Interim data, simulated mixing ratios of O₃, NO₂, HNO₃, ClO, HCl, and ClONO₂ by the MIROC3.2 CCM at 50 hPa for July 5 (day 186), August 19 (day 231), August 21 (day 233), and October 9 (day 282) in 2011. Polar vortex ~~edgesboundary~~ and location of Syowa Station were also plotted. On July 5 (day 186), the situation was similar to that of June 24 (day 175) in 2007. Note that inner edge of the polar vortex was defined on this day. Syowa Station was located deeper inside the polar vortex on July 5 in 2011 than on June 24 in 2007 and remaining HCl was observed by MLS (see Figure 5).

On August 19 (day 231) and August 21 (day 233), the situations were similar to those of September 2 (day 245) and September 6 (day 249) in 2007, respectively. ClO and ClONO₂ correlations on these days are also indicated by circles with crosses in Figure 10 (b).

On October 9 (day 282), the situation was similar to that of October 6 (day 279) in 2007, but Syowa Station was located inside the polar vortex closer to the inner vortex edge than in 2007. The recovery of ClONO₂ by reaction (R12) was simulated and observed at Syowa Station besides the recovery of HCl by reaction (R13), because there were some O₃ and NO₂ near the inner vortex edge (see Figure 5). This shows the phenomena described on the last paragraph in Section 4.2.

4.6 Time evolution of chlorine species from CCM and discussion

Three-hourly time series of zonal-mean active chlorine species, Cl₂O₂ (b), Cl₂ (c), ClO (d), and their sum (ClO+2*Cl₂O₂+2*Cl₂) (a), HOCl (e), and chlorine reservoir species HCl (fe) and ClONO₂ (gf) modeled by MIROC3.2 CCM at 68.4°S, 71.2°S, 76.7°S, and 87.9°S in 2007 are plotted in Figure 15. The dates on which the distribution of each species is shown in Figure 13 are indicated by vertical dotted lines. In Figure 15, it is shown that HCl and ClONO₂ rapidly decreased at around May 10 (day 130) at 87.9°S, when PSCs started to form in the Antarctic polar vortex (Figures 15(fe) and 15(gf)). The decrease of HCl stopped when the counter-part of the heterogeneous reaction (R1) (ClONO₂) was missing at around May 20 (day 140). Consequently, Cl₂ was formed (Figure 15(c)). Similar chlorine activation was seen at 76.7°S about 5-10 days later than at 87.9°S. Gradual conversion from Cl₂ into Cl₂O₂ (ClO-dimer) was seen at all latitudes at around May 30-June 9 (day 150-160) (Figures 15(b) and 15(c)) through reactions (R5), (R8), and (R9). At 87.9°S, conversion from Cl₂ to Cl₂O₂ was slow, due to lack of sunlight which is needed for reaction (R5). Increase of ClO occurred much later in winter (July 9; day 190 or later), because sun light is needed to form ClO by reactions (R5) and (R8) in the polar vortex (Figure 15(d)). Nevertheless, there were some enhancements of ClO in early winter, June 24 (day 175), simulated at the edge of the polar vortex (Figure 13) where there was some sunlight available due to the distortion of the shape of the polar vortex. Increase of ClO occurred from lower latitude (68.4°S) at around July 14 (day 195), towards higher latitude (87.9°S) at around ~~September 12~~August 13 (day 255) (Figure 15(d)). Diurnal variation of ClO was also seen at latitudes between 68.4°S and 76.7°S. When the stratospheric temperature increased above PSC saturation temperature at around September 27 (day 270) (Figure 3(ba)), chlorine activation ended, and ClO was mainly converted into HCl at all latitudes inside the polar vortex (Figures 15(d) and 15(fe)). This is because reactions (R13) and/or (R14) occurs more frequently than reaction (R12) inside the polar vortex due to the depleted O₃ amount there as was described in Section 1 (Douglass et al., 1995). Increase of HOCl due to heterogeneous reaction (R2) on the surface of PSCs occurred gradually from June at lower latitudes (68.4°S and 71.2°S) (Figure 15(e)). It also occurred at 76.7°S from July, and at 87.9°S from August. The cause of HOCl increase at 87.9°S from August is not clear at the moment. In Figure 15, the species which decreased at 87.9°S from August was Cl₂ (Figure 15 (c)). If sunlight was available, Cl₂ was converted into HOCl through reactions (R5), (R8), and the following reaction



Here, HO₂ was needed to yield HOCl. One possibility to yield HO₂ in August is either one of “HCl null cycles” C1 or C2, or chemical cycles C3 or C4 which was described in Müller et al. (2018).

Continuous loss of HCl was seen at 87.9°S between June 9 (day 160) and July 19 (day 200) even after the disappearance of the counterpart of heterogeneous reaction (R1) (Figure 15(~~fe~~)). The cause of this continuous loss was unknown until recently, where a hypothesis was proposed that includes the effect of decomposition of particulate HNO₃ by some process like ionisation caused by galactic cosmic rays during the winter polar vortex (Grooß et al., 2018). Solomon et al. (2015) proposed a ~~transport~~^{new} mechanism on this issue: Continuous transport of ClONO₂ from the sun-rich subpolar regions near 55-65°S to higher latitudes near 65-75°S provides a flux of NO_x from more sunlit latitudes into the polar vortex. Jaeglé et al. (1997) also described similar mechanism for HCl loss near the vortex edge with ER-2 Observations. They explained that the loss of HCl was caused by the excursions of air parcels in and out of sunlight during the winter, which photochemically resupply ClONO₂ and HOCl. Our result is partly consistent with the mechanism proposed by Solomon et al. (2015), which was indicated by some sporadic increase in ClONO₂ at around June 7 (day 158), June 28 (day 179), and July 8 (day 189) at 76.7°S as shown in Figure 15(~~gf~~). Subsequently, HCl losses were observed at 76.7°S and 87.9°S during these episodes in Figure 15(~~fe~~). Thus, the continuous loss of HCl at the most polar latitude (87.9°S) can be due to the gradual mixing of air within the polar vortex during the winter period, when polar vortex was still strong. However, we are not sure if such transport really occurs and affect the HCl loss at the core of the polar vortex. Another explanation of the loss of HCl is by heterogeneous reaction (R4) on the surface of PSCs with HOCl. Spiky increase of HOCl at 76.7°S and 87.9°S, and simultaneous decrease of HCl was occurred at around July 7 (day 188) and July 20 (day 201) in Figures 15(e) and 15(f). Continuous loss of HCl at the core of the polar vortex in August and September was recently proposed by Müller et al. (2018), that chemical cycles C3 and C4 are responsible for the decline of HCl in the vortex core. However, these chemical cycles require sun light to occur, which may not be available in June and July at the vortex core.

Recently, there was a discussion on “race” between chlorine activation and deactivation to maintain enhanced levels of active chlorine during the time period (September and early October) when rapid ozone loss occurs. Müller et al. (2018) proposed a so-called “HCl null-cycles” to keep enhanced chlorine levels. They proposed a mechanism that the formation HCl (R13) is followed by immediate reactivation of HCl by null-cycles C1 and C2 (Müller et al., 2018). Our MIROC3.2 CCM model results support the mechanism by high ClO and HOCl levels in September as shown in Figures 15(d) and 15(e).

5. Conclusions

Lower stratospheric vertical profiles of O₃, HNO₃, and HCl were retrieved using SFIT2 from solar spectra taken with a ground-based FTIR installed at Syowa Station, Antarctica from March to December 2007 and September to November 2011. This was the first continuous measurements of chlorine species throughout the ozone hole period from the ground in Antarctica.

Retrieved profiles were validated with Aura/MLS and ozonesonde data. The absolute differences between FTIR and Aura/MLS or ozonesonde measurements were within measurement error bars at the altitudes of interest.

To study the temporal variation of chlorine partitioning and ozone destruction from fall to spring in the Antarctic polar vortex, we analyzed temporal variations of measured minor species by FTIR over Syowa Station combined with satellite measurements of ClO, HCl, ClONO₂ and HNO₃. When the stratospheric temperature over Syowa Station fell ~~~4K~~^{well} below NAT PSC saturation temperature, PSCs started to form and heterogeneous reaction between HCl and ClONO₂ occurred and ClONO₂ was almost completely depleted at both 18 km and 22 km in early winter. When the sun came back to the Antarctic in spring, enhancement of ClO and gradual O₃ destruction were observed. During the ClO enhanced period, negative correlation between ClO and ClONO₂ was observed in the time-series of the data at Syowa Station. This negative correlation is associated with the relative distance between Syowa Station and the ~~inner~~-edge of the polar vortex.

To see the comprehensive behavior of chlorine and related species inside the polar vortex and the boundary region in more detail, results of MIROC3.2 CCM simulation were analyzed. Direct comparison between CCM results and observations show good day-to-day agreement in general, although some species show systematic differences especially at 18 km. The modeled O₃ is in good agreement with FTIR and satellite observations. Rapid conversion of chlorine reservoir species (HCl and ClONO₂) into Cl₂, gradual conversion of Cl₂ into Cl₂O₂, increase of HOCl in winter period, increase of ClO when sunlight became available, and conversion of ClO into HCl were successfully reproduced by the CCM. HCl decrease in the winter polar vortex core continued to occur due to either the transport of ClONO₂ from the subpolar region to higher latitudes, providing a flux of ClONO₂ from more sunlit latitudes into the polar vortex or the heterogeneous reaction with HOCl. Temporal variation of chlorine species over Syowa Station was affected both by heterogeneous chemistry related to PSC occurrence ~~deep~~ inside the polar vortex, and transport of NO_x-rich air mass from ~~lower latitudinal~~^{the} polar vortex boundary region, which can produce additional ClONO₂ by reaction (R12).

The deactivation pathways from active ClO into reservoir species (HCl and/or ClONO₂) were confirmed~~found~~ to be very dependent on the availability of ambient O₃. At an altitude (18 km) where most ozone was depleted in the Antarctic, most ClO was converted to HCl. However, at an altitude (22 km) when there was some O₃ available, additional increase of ClONO₂ than pre-winter value can occur, as in the case in the Arctic, through reactions (R15) and (R12) (Douglass et al., 1995; Groöß et al., 1997).

Data availability: The FTIR data presented here can be obtained in electronic form (hdf files) from the following DOIs:

doi:10.17595/20190911.001 (FTIR data for 2007).

doi:10.17595/20190911.002 (FTIR data for 2011).

The MIROC3.2 CCM outputs are from the REF-C1SD simulation data from the CCMI, which are stored at the CCMI site of BADC at:

<http://badc.nerc.ac.uk/browse/badc/wcrp-ccmi/data/CCMI-1/output/NIES>.

Author contributions. HN, IM, YN, and MT conceived and worked on the current research project. HN, KS, and TK made FTIR observations at Syowa Station in 2007 and 2011. HN, YN, KS, and NBJ conducted the SFIT2 retrievals. HA conducted MIROC3.2 CCM simulations and ED analysed them. YT performed polar vortex categorization calculation. HN, IM, YN, HA, YT, and NBJ contributed to the interpretation of the results and wrote the paper.

Competing interests. The authors declare that they have no competing financial interests.

Appendix A: MIROC3.2 nudged chemistry–climate model

The chemistry–climate model (CCM) used in this study was MIROC3.2 CCM, which was developed on the basis of version 3.2 of the Model for Interdisciplinary Research on Climate (MIROC3.2) general circulation model (GCM). The MIROC3.2 CCM introduces the stratospheric chemistry module of the old version of the CCM that was used for simulations proposed by the chemistry–climate model validation (CCMVal) and the second round of CCMVal (CCMVal2) (WMO, 2007, 2011; SPARC CCMVal, 2010; Akiyoshi et al., 2009, 2010). The MIROC3.2 CCM is a spectral model with a T42 horizontal resolution ($2.8^\circ \times 2.8^\circ$) and 34 vertical atmospheric layers above the surface. The top layer is located at approximately 80 km (0.01 hPa). Hybrid sigma–pressure coordinates are used for the vertical coordinate. The horizontal wind velocity and temperature in the CCM were nudged toward the ERA–Interim data (Dee et al., 2011) to simulate global distributions of ozone and other chemical constituents on a daily basis. The transport is calculated by a semi–Lagrangian scheme (Lin and Rood, 1996). The chemical constituents included in this model are O_x , HO_x , NO_x , ClO_x , BrO_x , hydrocarbons for methane oxidation, heterogeneous reactions [on the surface](#) for sulfuric-acid aerosols, supercooled ternary solutions, nitric-acid trihydrate, and ice particles. The CCM contains 13 heterogeneous reactions on multiple aerosol types ([Akiyoshi, 2007](#)) as well as gas-phase chemical reactions and photolysis reactions. [The surface of the particles for the heterogeneous reactions are calculated from the volume of condensation, assuming number density of the particles and the size distributions. Sedimentation of the particles is considered.](#) The reaction-rate and absorption coefficients are based on JPL–2010 (Sander et al., 2011). [Family method is used to calculate gas phase chemical reactions. The time integrations for the families and heterogeneous reactions are performed explicitly. The time step for the chemistry scheme is 6 minutes. A scheme of spherical geometry for radiation transfer was developed \(Kurokawa et al., 2005\) and used for radiation transfer calculation in the CCM. The photolysis rates of chemical constituents are calculated online, using the radiation flux in the CCM with 32 spectral bins.](#) See Akiyoshi et al. (2016) [and Supplement of Morgenstern et al. \(2017\)](#) for more details.

Appendix B: Determined polar vortex edges

Inner and outer edges of the polar vortex were determined as follows:

1) Equivalent latitudes (EL) (McIntyre and Palmer, 1984; Butchart and Remsberg, 1986) were computed based on isentropic potential vorticity at 450 K and 560 K isentropic surfaces for 18 km and 22 km using the ERA-Interim reanalysis data (Dee et al., 2011), respectively.

2) Inner and outer edges (at least 5° apart from each other) of the polar vortex were defined by local maxima of the isentropic potential vorticity gradient with respect to equivalent latitude only when a tangential wind speed (i.e., mean horizontal wind speed along the isentropic potential vorticity contour; see Eq. (1) of Tomikawa and Sato (2003)) near the vortex edge exceeds a threshold value (i.e., 20 m s⁻¹, see Nash et al. (1996) and Tomikawa et al. (2015)).

3) Then, the polar region was divided into three regions; i.e., inside the polar vortex (inside of inner edge), the boundary region (between inner and outer edges), and outside the polar vortex (outside of outer edge) when there were two polar vortex edges. When there was only one edge, the polar region was divided into two regions; i.e., inside the polar vortex and outside the polar vortex.

Figures A1 and A2 show time-equivalent latitude sections of modified potential vorticity (MPV) and its gradient with respect to EL at 450 and 560 K isentropic potential temperature (PT) surfaces in 2007 and 2011, respectively. MPV is a scaled PV to remove its exponential increase with height (cf., Lait, 1994). The inner and outer edge(s) are plotted by black dots, while the ELs of Syowa Station on those days are plotted by red dots. It can be seen that inner edges were first formed at around EL of 70 degrees in April, and outer edges started to form at around EL of 55 degrees in July-August, emerging the boundary region. Then, those two edges converge into one edge at around EL of 60 degrees in November. Finally, the polar vortex edge disappeared in December. Syowa Station was mostly located inside the polar vortex, but sometimes located at the boundary region or outside the polar vortex, depending on different PT levels.

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References

- ~~Anderson, J., Russell, J. M., III, Solomon, S., and Deaver, L. E.: Halogen Occultation Experiment confirmation of stratospheric chlorine decreases in accordance with the Montreal Protocol, J. Geophys. Res., 105, 4483-4490, doi:10.1029/1999JD901075, 2000.~~
- 5 [Akiyoshi, H.: Modeling of the heterogeneous reaction processes on the polar stratospheric clouds in chemical transport models and the effects on the Arctic ozone layer through bromine species, Earozoru Kenkyu, 22, 196-203, 2007 \(in Japanese\).](#)
- Akiyoshi, H., Zhou, L. B., Yamashita, Y., Sakamoto, K., Yoshiki, M., Nagashima, T., Takahashi, M., Kurokawa, J., Takigawa, M., and Imamura, T.: A CCM simulation of the breakup of the Antarctic polar vortex in the years 1980–2004 under the CCMVal scenarios, J. Geophys. Res., 114, D03103(1–28), doi:10.1029/2007JD009261, 2009.
- 10 Akiyoshi, H., Y. Yamashita, K. Sakamoto, L. B. Zhou, and T. Imamura: Recovery of stratospheric ozone in calculations by the Center for Climate System Research/National Institute for Environmental Studies chemistry–climate model under the CCMVal–REF2 scenario and a no–climate–change run, J. Geophys. Res., 115, D19301(1–22), doi:10.1029/2009JD012683, 2010.
- Akiyoshi, H., Nakamura, T., Miyasaka, T., Shiotani, M., and Suzuki, M.: A nudged chemistry–climate model simulation of
- 15 chemical constituent distribution at northern high-latitude stratosphere observed by SMILES and MLS during the 2009/2010 stratospheric sudden warming, J. Geophys. Res. Atmos., 121, 1361-1380, doi:10.1002/2015JD023334, 2016.
- Anderson, J. G., Brune, W. H., and Proffitt, M. H.: Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of ClO–O₃ anticorrelation based on in situ ER-2 data, J. Geophys. Res., 94, 11,465-11479, 1989.
- 20 Anderson, J., Russell, J. M., III, Solomon, S., and Deaver, L. E.: Halogen Occultation Experiment confirmation of stratospheric chlorine decreases in accordance with the Montreal Protocol, J. Geophys. Res., 105, 4483-4490, doi:10.1029/1999JD901075, 2000.
- ~~Blumenstock, T., Kopp, G., Hase, F., Hochschild, G., Mikuteit, S., Raffalski, U., and Ruhnke, R.: Observation of unusual chlorine activation by ground-based infrared and microwave spectroscopy in the late Arctic winter 2000/01, Atmos. Chem. Phys., 6, 897-905, 2006.~~
- 25 [Bonne, G. P., Stimpfle, R. M., Cohen, R. C., Voss, P. B., Perkins, K. K., Anderson, J. G., Salawitch, R. J., Elkins, J. W., Dutton, G. S., Jucks, K. W., and Toon, G. C.: An examination of the inorganic chlorine budget in the lower stratosphere, J. Geophys. Res., 105, D2, 1957-1971, 2000.](#)
- Butchart, N., and Remsberg, E. E.: The area of the stratospheric polar vortex as a diagnostic for tracer transport on an isentropic surface, J. Atmos. Sci., 43, 1319–1339, 1986.
- 30 Canty, T. P., Salawitch, R. J., and Wilmouth, D. M.: The kinetics of the ClOOCl catalytic cycle, J. Geophys. Res., 121, 13,768-13, 783, doi:10.1002/2016JD025710, 2016.

- Chubachi, S.: Preliminary result of ozone observation at Syowa Station from February 1982 to January 1983, Mem. Natl Inst. Polar Res., Spec. Issue, 34, 13-19, 1984.
- Connor, B., Parrish, A., Tsou, J., and McCormick, M.: Error analysis for the ground-based microwave ozone measurements during STOIC, J. Geophys. Res., 100, 9283-9291, 1995.
- 5 de Laat, A. T. J., van Weele, M., and van der A, R. J.: Onset of stratospheric ozone recovery in the Antarctic ozone hole in assimilated daily total ozone columns, J. Geophys. Res., 122, 11,880-11,899, doi:10.1002/2016JD025723, 2017.
- de Zafra, R. L., Jaramillo, M., Barrett, J., Emmons, L. K., Solomon, P. M., and Parrish, A.: New observations of a large concentration of ClO in the springtime lower stratosphere over Antarctica and its implications for ozone-depleting chemistry, J. Geophys. Res., 94, D9, 11,423-11,428, 1989.
- 10 Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J. -J., Park, B. -K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J. -N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Q. J. R.
- 15 Meteorol. Soc., 137, 553–597, doi:10.1002/qj.828, 2011.
- Douglass, A. R., Schoeberl, M. R., Stolarski, R. S., Waters, J. W., Russell, J. M., III, Roche, A. E., and Massie, S. T.: Interhemispheric differences in springtime production of HCl and ClONO₂ in the polar vortices, J. Geophys. Res., 100, 13,967-13,978, 1995.
- Drdla, K. and Müller, R.: Temperature thresholds for chlorine activation and ozone loss in the polar stratosphere, Ann. Geophys., 30, 1055-1073, doi:10.5194/angeo-30-1055-2012, 2012
- 20 Dufour, G., Nassar, R., Boone, C. D., Skelton, R., Walker, K. A., Bernath, P. F., Rinsland, C. P., Semeniuk, K., Jin, J. J., McConnell, J. C., and Manney, G. L.: Partitioning between the inorganic chlorine reservoirs HCl and ClONO₂ during the Arctic winter 2005 from the ACE-FTS, Atmos. Chem. Phys., 6, 2355-2366, 2006.
- Farman, J. C., Gardiner, B. G., and Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, Nature, 315, 207-210, 1985.
- 25 Farmer, C. B., Toon, G. C., Schaper, P. W., Blavier, J. -F., and Lowes, L. L.: Stratospheric trace gases in the spring 1986 Antarctic atmosphere, Nature, 329, 126-130, 1987.
- Fischer, H., and Oelhaf, H.: Remote sensing of vertical profiles of atmospheric trace constituents with MIPAS limb-emission spectrometers, Appl. Opt., 35, 2787-2796, 1996.
- 30 Fischer, H., Birk, M., Blom, C., Carli, B., Carlotti, M., von Clarmann, T., Delbouille, L., Dudhia, A., Ehrt, D., Endemann, M., Flaud, J. M., Gessner, R., Kleinert, A., Koopmann, R., Langen, J., López-Puertas, M., Mosner, P., Nett, H., Oelhaf, H., Perron, G., Remedios, J., Ridolfi, M., Stiller, G., and Zander, R.: MIPAS: An instrument for atmospheric and climate research, Atmos., Chem. Phys., 8, doi:10.5194/acp-8-2151-2008, 2008.

- Froidevaux, L., et al.: Early validation analyses of atmospheric profiles from EOS MLS on the Aura satellite, IEEE Trans. Geosci. Remote Sens., 44, 1106-1121, 2006.
- 5 Froidevaux, L., Jiang, Y. B., Lambert, A., Livesey, N. J., Read, W. G., Waters, J. W., Browell, E. V., Hair, J. W., Avery, M. A., McGee, T. J., Twigg, L. W., Sumnicht, G. K., Jucks, K. W., Margitan, J. J., Sen, B., Stachnik, R. A., Toon, G. C., Bernath, P. F., Boone, C. D., Walker, K. A., Filipiak, M. J., Harwood, R. S., Fuller, R. A., Manney, G. L., Schwartz, M. J., Daffer, W. H., Drouin, B. J., Cofield, R. E., Cuddy, D. T., Jarnot, R. F., Knosp, B. W., Perun, V. S., Snyder, W. V., Stek, P. C., Thurstans, R. P., and Wagner, P. A.: Validation of Aura Microwave Limb Sounder stratospheric ozone measurements, J. Geophys. Res., 113, D15S20, doi:10.1029/2007JD008771, 2008.
- 10 Gallery, W. O., Kneizys, F. S., and Clough, S. A.: Air mass computer program for atmospheric transmittance/radiance calculation: FSCATM, Environmental Research Paper ERP-828/AFGL-TR-83-0065, Air Force Geophysical Laboratory, Bedford, MA, USA, 1983.
- Goldman, A., Fernald, F. G., Murcray, F. J., Murcray, F. H., and Murcray, D. G.: Spectral least squares quantification of several atmospheric gases from high resolution infrared solar spectra obtained at the South Pole, J. Quant. Spectrosc. Radiat. Transfer, 29, 189-204, 1983.
- 15 Goldman, A., Murcray, F. J., Murcray, F. H., and Murcray, D. G.: Quantification of HCl from high resolution infrared solar spectra obtained at the South Pole in December 1986, Geophys. Res. Lett., 14, 622-623, 1987.
- Groß, J. -U., Pierce, R. B., Crutzen, P. J., Grose, W. L., and Russell III, J. M.: Reformation of chlorine reservoirs in southern hemisphere polar spring, J. Geophys. Res., 102, 13,141-13,152, doi:10.1029/96JD03505, 1997.
- Groß, J. -U., Brauttsch, K., Pommrich, R., Solomon, S., and Müller, R.: Stratospheric ozone chemistry in the Antarctic: what determines the lowest ozone values reached and their recovery?, Atmos. Chem. Phys., 11, 12,217-12,226, doi:10.5194/acp-11-12217-2011, 2011.
- 20 Groß, J. -U., Müller, R., Spang, R., Tritscher, I., Wegner, T., Chipperfield, M. P., Feng, W., Kinnison, D. E., and Madronich, S.: On the discrepancy of HCl processing in the core of the wintertime polar vortices, Atmos. Chem. Phys., 18, 8647-8666, doi:10.5194/acp-18-8647-2018, 2018.
- 25 Hase, F., Hannigan, J. W., Coley, M. T., Goldman, A., Höpfner, M., Jones, N. B., Rinsland, C. P., Wood, S. W.: Intercomparison of retrieval codes used for the analysis of high-resolution, ground-based FTIR measurements, J. Quant. Spectrosc. Radiat. Transfer, 87, 25-52, 2004.
- Hayashida, S., Sugita, T., Ikeda, N., Toda, Y., and Irie, H.: Temporal evolution of ClONO₂ observed with Improved Limb Atmospheric Spectrometer (ILAS) during Arctic late winter and early spring in 1997, J. Geophys. Res., 112, D14311, doi:10.1029/2006JD008108, 2007.
- 30 Höpfner, M., von Clarmann, T., Fischer, H., Glatthor, N., Grabowski, U., Kellmann, S., Kiefer, M., Linden, A., Mengistu Tsidu, G., Milz, M., Steck, T., Stiller, G. P., Wang, D. Y., and Funke, B.: First spaceborne observations of Antarctic stratospheric ClONO₂ recovery: Austral spring 2002, J. Geophys. Res., 109, D11308, doi:10.1029/2004JD004609, 2004.

- Höpfner, M., von Clarmann, T., Fischer, H., Funke, B., Glatthor, N., Grabowski, U., Kellmann, S., Kiefer, M., Linden, A., Milz, M., Steck, T., Stiller, G. P., Bernath, P., Blom, C. E., Blumenstock, Th., Boone, C., Chance, K., Coffey, M. T., Friedl-Vallon, F., Griffith, D., Hannigan, J. W., Hase, F., Jones, N., Jucks, K. W., Keim, C., Kleinert, A., Kouker, W., Liu, G. Y., Mahieu, E., Mellqvist, J., Mikuteit, S., Notholt, J., Oelhaf, H., Piesch, C., Reddmann, T., Ruhnke, R., Schneider, M., Strandberg, A., Toon, G., Walker, K. A., Warneke, T., Wetzel, G., Wood, S., and Zander, R.: Validation of MIPAS ClONO₂ measurements, *Atmos. Chem. Phys.*, 7, 257-281, 2007.
- Jaeglé, L., Webster, C. R., May, R. D., Scott, D. C., Stimpfle, R. M., Kohn, D. W., Wennberg, P. O., Hanisco, T. F., Cohen, R. C., Proffitt, M. H., Kelly, K. K., Elkins, J., Baumgardner, D., Dye, J. E., Wilson, J. C., Pueschel, R. F., Chan, K. R., Salawitch, R. J., Tuck, A. F., Hovde, S. J., and Yung, Y. L.: Evolution and stoichiometry of heterogeneous processing in the Antarctic stratosphere, *J. Geophys. Res.*, 102, 13,235-13,253, 1997.
- Ko, M. K. W., Rodriguez, J. M., Sze, N. D., Proffitt, M. H., Starr, W. L., Krueger, A., Browell, E. V., McCormick, M. P.: Implications of AAOE observations for proposed chemical explanations of the seasonal and interannual behavior of Antarctic ozone, *J. Geophys. Res.*, 94, D14, 16,705-16,715, 1989.
- Komhyr, W. D.: Operations handbook – Ozone measurements to 40 km altitude with model 4A-ECC-ozone sondes, NOAA Techn. Memorandum ERL-ARL-149, 1986.
- Kreher, K., Keys, J. G., Johnston, P. V., Platt, U., and Liu, X.: Ground-based measurements of OCIO and HCl in austral spring 1993 at Arrival Heights Antarctica, *Geophys. Res. Lett.*, 23, 1545-1548, 1996.
- Kurokawa, J., Akiyoshi, H., Nagashima, T., Nakane, H., Masunaga, H., Nakajima, T., Takahashi, M.: Effects of atmospheric sphericity on the stratospheric chemistry and dynamics over Antarctica, *J. Geophys. Res.*, 110, D21305, doi:10.1029/2005JD005798, 2005.
- Kuttippurath, J., Goutail, F., Pommereau, J. -P., Lefèvre, F., Roscoe, H. K., Pazmiño, A., Feng, W., Chipperfield, M. P., and Godin-Beekmann, S.: Estimation of Antarctic ozone loss from ground-based total column measurements, *Atmos. Chem. Phys.*, 10, 6569-6581, 2010.
- Lait, L. R.: An alternative form for potential vorticity, *J. Atmos. Sci.*, 51, 1754-1759, 1994.
- Lee, A. M., Roscoe, H. K., Jones, A. E., Haynes, P. H., Shuckburgh, E. F., Morrey, M. W., and Pumphrey, H. C.: The impact of the mixing properties within the Antarctic stratospheric vortex on ozone loss in spring, *J. Geophys. Res.*, 106, D3, 3203-3211, doi:10.1029/2000JD900398, 2001.
- Lin, S.-J. and Rood, R. B.: Multidimensional flux-form semi-Lagrangian transport schemes, *Mon. Wea. Rev.*, 124, 2046-2070, 1996.
- Liversey, N., Van Snyder, W., Read, W., and Wagner, P.: Retrieval algorithms for the EOS Microwave Limb Sounder (MLS), *Geoscience and Remote Sensing, IEEE Transactions*, 44, 1144-1155, doi:10.1109/TGRS.2006.872327, 2006.
- Livesey, N. J., Read, W. G., Froidevaux, L., Lambert, A., Manney, G. L., Pumphrey, H. C., Santee, M. L., Schwartz, M. J., Wang, S., Cofield, R. E., Cuddy, D. T., Fuller, R. A., Jarnot, R. F., Jiang, J. H., Brian W. Knosp, Stek, P. C., Wagner, P.

- A., and Wu., D. L.: Version 3.3 and 3.4 Level 2 data quality and description document, Jet Propul. Lab., Tech. Rep. JPL D-33509, Pasadena, CA, USA (Available from <http://mls.jpl.nasa.gov>), 2013.
- Livesey, N. J., Read, W. G., Wagner, P. A., Froidevaux, L., Lambert, A., Manney, G. L., Millán Valle, L. F., Pumphrey, H. C., Santee, M. L., Schwartz, M. J., Wang, S., Fuller, R. A., Jarnot, R. F., Knosp, B. W., Martinez, E., and Lay, R. R.:
5 Version 4.2x Level 2 data quality and description document, Jet Propul. Lab., Tech. Rep. JPL D-33509 Rev. D, Pasadena, CA, USA (Available from <http://mls.jpl.nasa.gov>), 2018.
- Manney, G. L., Santee, M. L., Rex, M., Livesey, N. J., Pitts, M. C., Veefkind, P., Nash, E. R., Wohltmann, I., Lehmann, R., Froidevaux, L., Poole, L. R., Schoeberl, M. R., Haffner, D.P., Davies, J., Dorokhov, V., Gernandt, H., Johnson, B., Kivi, R., Kyrö, E., Larsen, N., Levelt, P. F., Makshtas, A., McElroy, C. T., Nakajima, H., Parrondo, M. C., Tarasick, D. W., von
10 der Gathen, P., Walker, K. A., and Zinoviev, N. S.: Unprecedented Arctic ozone loss in 2011, *Nature*, 478, 469-475, doi:10.1038/nature10556, 2011.
- McIntyre, M. E., and Palmer, T. N.: The ‘surf zone’ in the stratosphere, *J. Atmos. Terr. Phys.*, 46, 825–849, 1984.
- ~~Mellqvist, J., Galle, B., Blumenstock, T., Hase, F., Yasheov, D., Notholt, J., Sen, B., Blavier, J. F., Toon, G. C., and Chipperfield, M. P.: Ground-based FTIR observations of chlorine activation and ozone depletion inside the Arctic vortex during the winter of 1999/2000, *J. Geophys. Res.*, 107, D20, 8263, doi:10.1029/2001JD001080, 2002.~~
15 ~~during the winter of 1999/2000, *J. Geophys. Res.*, 107, D20, 8263, doi:10.1029/2001JD001080, 2002.~~
- Michelsen, H. A., Webster, C. R., Manney, G. L., Scott, D. C., Margitan, J. J., May, R. D., Irion, F. W., Gunson, M. R., Russell III, J. M., and Spivakovsky, C. M.: Maintenance of high HCl/Cl_y and NO_x/NO_y in the Antarctic vortex: A chemical signature of confinement during spring, *J. Geophys. Res.*, 104, 26,419-26,436, 1999.
- [Morgenstern, O., Hegglin, M. I., Rozanov, E., O’Connor, F. M., Abraham, N. L., Akiyoshi, H., Archibald, A. T., Bekki, S., Butchart, N., Chipperfield, M. P., Deushi, M., Dhomse, S. S., Garcia, R. R., Hardiman, S. C., Horowitz, L. W., Jöckel, P., Josse, B., Kinnison, D., Lin, M. Y., Mancini, E., Manyin, M. E., Marchand, M., Marécal, V., Michou, M., Oman, L. D., Pitari, G., Plummer, D. A., Revell, L. E., Saint-Martin, D., Schofield, R., Stenke, A., Stone, K., Sudo, K., Tanaka, T. Y., Tilmes, S., Yamashita, Y., Yoshida, and K., Zeng, G.: Review of the global models used within phase 1 of the Chemistry-Climate Model Initiative \(CCMI\), *Geosci. Model Dev.*, 10, 639-671, doi:10.5194/gmd-10-639-2017, 2017.](#)
20 [Butchart, N., Chipperfield, M. P., Deushi, M., Dhomse, S. S., Garcia, R. R., Hardiman, S. C., Horowitz, L. W., Jöckel, P., Josse, B., Kinnison, D., Lin, M. Y., Mancini, E., Manyin, M. E., Marchand, M., Marécal, V., Michou, M., Oman, L. D., Pitari, G., Plummer, D. A., Revell, L. E., Saint-Martin, D., Schofield, R., Stenke, A., Stone, K., Sudo, K., Tanaka, T. Y., Tilmes, S., Yamashita, Y., Yoshida, and K., Zeng, G.: Review of the global models used within phase 1 of the Chemistry-Climate Model Initiative \(CCMI\), *Geosci. Model Dev.*, 10, 639-671, doi:10.5194/gmd-10-639-2017, 2017.](#)
- Müller, R., Peter, T., Crutzen, P. J., Oelhaf, H., Adrian, G. P., v. Clarmann, T., Wegner, A., Schmidt, U., and Lary, D.: Chlorine chemistry and the potential for ozone depletion in the Arctic stratosphere in the winter of 1991/92, *Geophys. Res. Lett.*, 21, 1427-1430, 1994.
- Müller, R., Crutzen, P. J., Groöf, J. -U., Brühl, C., Russell III, J. M., and Tuck, A. F.: Chlorine activation and ozone depletion in the Arctic vortex: Observations by the Halogen Occultation Experiment on the Upper Atmosphere Research
30 Satellite, *J. Geophys. Res.*, 101, D7, 12,531-12,554, 1996.
- [Müller, R., Groöf, J. -U., Zafar, A. M., Robrecht, S., and Lehmann, R.: The maintenance of elevated chlorine levels in the Antarctic lower stratosphere through HCl null cycles, *Atmos. Chem. Phys.*, 18, 2985-2997, doi:10.5194/acp-18-2985-2018, 2018.](#)

- [Murcray, F. J., Murcray, F. H., Goldman, A., and Murcray, D. G.: Infrared measurements of several nitrogen species above the South Pole in December 1980 and November-December 1986, J. Geophys. Res., 92, D11, 13,373-13,376, 1987.](#)
- [Murcray, F. J., Goldman, A., Blatherwick, R., Matthews, A., and Jones, N. B.: HNO₃ and HCl amounts over McMurdo during the spring of 1987, J. Geophys. Res., 94, D14, 16,615-16,618, 1989.](#)
- 5 Nakajima, H.: Preface to special section on ILAS-II: The Improved Limb Atmospheric Spectrometer II, J. Geophys. Res., 111, D20S90, doi:10.1029/2006JD007412, 2006.
- Nakajima, H., Sugita, T., Yokota, T., Ishigaki, T., Mogi, Y., Araki, N., Waragai, K., Kimura, N., Iwazawa, T., Kuze, A., Tanii, J., Kawasaki, H., Horikawa, M., Togami, T., Uemura, N., Kobayashi, H., and Sasano, Y.: Characteristics and performance of the Improved Limb Atmospheric Spectrometer-II (ILAS-II) on board the ADEOS-II satellite, J. Geophys. Res., 111, D11S01, doi:10.1029/2005JD006334, 2006.
- 10 Nakajima, H., Wohltmann, I., Wegner, T., Takeda, M., Pitts, M. C., Poole, L. R., Lehmann, R., Santee, M. L., and Rex, M.: Polar stratospheric cloud evolution and chlorine activation measured by CALIPSO and MLS, and modeled by ATLAS, Atmos. Chem. Phys., 16, 3311-3325, doi:10.5194/acp-16-3311-2016, 2016.
- Nash, E. R., Newman, P. A., Rosenfield, J. E., and Schoeberl, M. R.: An objective determination of the polar vortex using Ertel's potential vorticity, J. Geophys. Res., 101, 9471-9478, 1996.
- 15 [Newman, P. A., Daniel, J. S., Waugh, D. W., and Nash, E. R.: A new formulation of equivalent effective stratospheric chlorine \(EESC\), Atmos. Chem. Phys., 7, 4537-4552, doi:10.5194/acp-7-4537-2007, 2007.](#)
- Norton, R., and Rinsland, C.: ATMOS data processing and science analysis methods, Appl. Opt., 30, 389-400, 1991.
- Oelhaf, H., v. Clarmann, T., Fischer, H., Friedl-Vallon, F., Fritzsche, C., Linden, A., Piesch, C., Seefeldner, M., and Völker, W.: Stratospheric ClONO₂ and HNO₃ profiles inside the Arctic vortex from MIPAS-B limb emission spectra obtained during EASOE, Geophys. Res. Lett., 21, 1263-1266, doi:10.1029/93GL01303, 1994.
- 20 Parrish, A., Connor, B., Tsou, J., McDermid, I., and Chu, W.: Ground-based microwave monitoring of stratospheric ozone, J. Geophys. Res., 97, 2541-2546, 1992.
- Pitts, M. C., Thomason, L. W., Poole, L. R., and Winker, D. M.: Characterization of Polar Stratospheric Clouds with spaceborne lidar: CALIPSO and the 2006 Antarctic season, Atmos. Chem. Phys., 7, 5207-5228, doi:10.5194/acp-7-5207-2007, 2007.
- 25 Pitts, M. C., Poole, L. R., and Thomason, L. W.: CALIPSO polar stratospheric cloud observations: second-generation detection algorithm and composition discrimination, Atmos. Chem. Phys., 9, 7577-7589, doi:10.5194/acp-9-7577-2009, 2009.
- Pitts, M. C., Poole, L. R., Dörnbrack, A., and Thomason, L. W.: The 2009-2010 Arctic polar stratospheric cloud season: a CALIPSO perspective, Atmos. Chem. Phys., 11, 2161-2177, doi:10.5194/acp-11-2161-2011, 2011.
- 30 Rees, D., Barnett, J. J., and Labitzke, K.: COSPAR International Reference Atmosphere: 1986, Part II, Middle Atmosphere Models, Adv. Space Res., 10, 1-525, 1990.
- [Rinsland, C. P., Goldman, A., Murcray, F. J., Murcray, F. H., Blatherwick, R. D., and Murcray, D. G.: Infrared measurements of atmospheric gases above Mauna Loa, Hawaii, in February 1987, J. Geophys. Res., 93, 12,607-12,626, 1988](#)

- Rinsland, C. P., Jones, N. B., Connor, B. J., Logan, J. A., Pougatchev, N. S., Goldman, A., Murcray, F. J., Stephen, T. M., Pine, A. S., Zander, R., Mahieu, E., and Demoulin, P.: Northern and Southern Hemisphere ground-based infrared spectroscopic measurements of tropospheric carbon monoxide and ethane, *J. Geophys. Res.*, 103, 28,197-28,218, 1998.
- Rodgers, C. D.: *Inverse methods for atmospheric sounding: Theory and practice.*, World Scientific, Singapore, 2000.
- 5 Saitoh, N., Hayashida, S., Sugita, T., Nakajima, H., Yokota, T., Hayashi, M., Shiraishi, K., Kanzawa, H., Ejiri, M. K., Irie, H., Tanaka, T., Terao, Y., Bevilacqua, R. M., Randall, C. E., Thomason, L. W., Taha, G., Kobayashi, H., and Sasano, Y.: Intercomparison of ILAS-II version 1.4 aerosol extinction coefficient at 780 nm with SAGE II, SAGE III, and POAM III, *J. Geophys. Res.*, 111, D11S05, doi:10.1029/2005JD006315, 2006.
- Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M.
- 10 J., Moortgat, G. K., Orkin, V. L. and Wine, P. H.: *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, <http://jpldataeval.jpl.nasa.gov/>, 2011.
- Santee, M. L., Manney, G. L., Waters, J. W., and Livesey, N. J.: Variations and climatology of ClO in the polar lower stratosphere from UARS Microwave Limb Sounder measurements, *J. Geophys. Res.*, 108, D15, 4454, doi:10.1029/2002JD003335, 2003.
- 15 Santee, M. L., MacKenzie, I. A., Manney, G. L., Chipperfield, M. P., Bernath, P. F., Walker, K. A., Boone, C. D., Froidevaux, L., Livesey, N. J., and Waters, J. W.: A study of stratospheric chlorine partitioning based on new satellite measurements and modeling, *J. Geophys. Res.*, 113, D12307, doi:10.1029/2007JD009057, 2008.
- Santee, M. L., Manney, G. L., Livesey, N. J., Froidevaux, L., Schwartz, M. J., and Read, W. G.: Trace gas evolution in the
- 20 lowermost stratosphere from Aura Microwave Limb Sounder measurements, *J. Geophys. Res.*, 116, D18306, doi:10.1029/2011JD0015590, 2011.
- [Schauffler, S. M., Atlas, E. L., Donnelly, S. G., Andrews, A., Montzka, S. A., Elkins, J. W., Hurst, D. F., Romashkin, P. A., Dutton, G. S., and Stroud, V.: Chlorine budget and partitioning during the Stratospheric Aerosol and Gas Experiment \(SAGE\) III Ozone Loss and Validation Experiment \(SOLVE\), *J. Geophys. Res.*, 108, 4173, doi:10.1029/2001JD002040, 2003.](#)
- 25 [Schneider, M., Hase, F., Blumenstock, T., Redondas, A., and Cuevas, E.: Quality assessment of O₃ profiles measured by a state-of-the-art ground-based FTIR observing system, *Atmos. Chem. Phys.*, 8, 5579-5588, doi:10.5194/acp-8-5579-2008, 2008.](#)
- [Smit, H. G. J. and Straeter, W.: JOSIE-2000, Jülich Ozone Sonde Intercomparison Experiment 2000, The 2000 WMO international intercomparison of operating procedures for ECC-ozone sondes at the environmental simulation facility at Jülich, WMO Global Atmosphere Watch report series, No. 158, World Meteorological Organization, Geneva, 2004.](#)
- 30 Solomon, S., Garcia, R. R., Rowland, F. S., and Wuebbles, D. J.: On the depletion of Antarctic ozone, *Nature*, 321, 755-758, 1986.

- [Solomon, S., Mount, G. H., Sanders, R. W., and Schmeltekopf, A. L.: Visible spectroscopy at McMurdo Station, Antarctica, 2. Observations of OClO, J. Geophys. Res., 92, 8329-8338, 1987.](#)
- ~~Solomon, S., Borrmann, S., Garcia, R. R., Portmann, R., Thomason, L., Poole, L. R., Winker, D., and McCormick, M. P.: Heterogeneous chlorine chemistry in the tropopause region, J. Geophys. Res., 102, 21,411-21,429, 1997.~~
- 5 Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, Rev. Geophys., 37, 275-316, doi:10.1029/1999RG900008, 1999
- Solomon, S., Kinnison, D., Bandoro, J., and Garcia, R.: Simulation of polar ozone depletion: An update, J. Geophys. Res., 120, 7958-7974, doi:10.1002/2015JD023365, 2015.
- Solomon, S., Ivy, D. J., Kinnison, D., Mills, M. J., Neely III, R. R., and Schmidt, A.: Emergence of healing in the Antarctic
- 10 ozone layer, Science, doi:10.1126/science.aae0061, 2016.
- SPARC CCMVal: SPARC Report on the Evaluation of Chemistry–Climate Models, V. Eyring, T. G. Shepherd, and D. W. Waugh (Eds.), SPARC Report No.5, WCRP–132, WMO/TD–No.1526, 2010.
- [Strahan, S. E., Douglass, A. R., Newman, P. A., and Steenrod, S. D.: Inorganic chlorine variability in the Antarctic vortex and implications for ozone recovery, J. Geophys. Res. Atmos., 119, 14,098-14,109, doi:10.1002/2014JD022295, 2014.](#)
- 15 Sugita, T., Nakajima, H., Yokota, T., Kanzawa, H., Gernandt, H., Herber, A., von der Gathen, P., König-Langlo, G., Sato, K., Dorokhov, V., Yushkov, V. A., Murayama, Y., Yamamori, M., Godin-Beekmann, S., Goutail, F., Roscoe, H. K., Deshler, T., Yela, M., Taalas, P., Kyrö, E., Oltmans, S. J., Johnson, B. J., Allaart, M., Litynska, Z., Klekociuk, A., Andersen, S. B., Braathen, G. O., De Backer, H., Randall, C. E., Bevilacqua, R. M., Taha, G., Thomason, L. W., Irie, H., Ejiri, M. K., Saitoh, N., Tanaka, T., Terao, Y., Kobayashi, H., and Sasano, Y.: Ozone profiles in the high-latitude stratosphere and lower
- 20 mesosphere measured by the Improved Limb Atmospheric Spectrometer (ILAS)-II: Comparison with other satellite sensors and ozonesondes, J. Geophys. Res., 111, D11S02, doi:10.1029/2005JD006439, 2006.
- [Tilmes, S., Müller, R., Groö, J. -U., Nakajima, H., and Sasano, Y., J. Geophys. Res., 111, D24S90, doi:10.1029/2005JD006726, 2006.](#)
- Tomikawa, Y., and Sato, K.: Trapped waves in the edge region of stratospheric polar vortices, J. Geophys. Res., 108, 4047,
- 25 doi:10.1029/2002JD002579, 2003.
- Tomikawa, Y., Sato, K., Hirasawa, N., Tsutsumi, M., and Nakamura, T.: Balloon-borne observations of lower stratospheric water vapor at Syowa Station, Antarctica in 2013, Polar Sci., 9, 345–353, doi:10.1016/j.polar.2015.08.003, 2015.
- Tuck, A. F., Kelly, K. K., Webster, C. R., Loewenstein, M., Stimpfle, R. M., Proffitt, M. H., and Chan, R. K.: Airborne chemistry and dynamics at the edge of the 1994 Antarctic vortex, J. Chem. Soc. Faraday Trans., 91, 3063-3071, 1995.
- 30 von Clarmann, T. and Johansson, S.: Chlorine nitrate in the atmosphere, Atmos. Chem. Phys., 18, 15,363-15,386, doi:10.5194/acp-18-15363-2018, 2018.
- von Clarmann, T., Fischer, H., Friedl-Vallon, F., Linden, A., Oelhaf, H., Piesch, C., Seefeldner, M., and Völker, W.: Retrieval of stratospheric O₃, HNO₃, and ClONO₂ profiles from 1992 MIPAS-B limb emission spectra: method, results and error analysis, J. Geophys. Res., 98, 20,495-20,506, 1993.

- von Clarmann, T., Glatthor, N., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Tsidu, G. M., Milz, M., Steck, T., Stiller, G. P., Wand, D. Y., and Fischer, H.: Retrieval of temperature and tangent altitude pointing from limb emission spectra recorded from space by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), *J. Geophys. Res.*, 108, 4736, doi:10.1029/2003JD003602, 2003.
- 5 Waters, J. W., et al.: The Earth Observing System Microwave Limb Sounder (EOS MLS) on the Aura satellite, *IEEE Trans. Geosci. Remote Sens.*, 44, 1075-1092, 2006.
- Wegner, T., Grooß, J. -U., vonHobe, M., Stroh, F., Sumińska-Ebersoldt, O., Volk, C. M., Hösen, E., Mitev, V., Shur, G., and Müller, R.: Heterogeneous chlorine activation on stratospheric aerosols and clouds in the Arctic polar vortex, *Atmos. Chem. Phys.*, 12, 11,095-11,106, doi:10.5194/acp-12-11095-2012, 2012.
- 10 Winker, D. M., McGill, M., and Hunt, W. H.: Initial performance assessment of CALIOP, *Geophys. Res. Lett.*, 34, L19803, doi:10.1029/2007GL30135, 2007.
- WMO: Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project—Report No. 50, 572 pp., Geneva, Switzerland, 2007.
- WMO: Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project—Report No. 52, 15 516 pp., Geneva, Switzerland, 2011.
- WMO: Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project—Report No. 55, 416 pp., Geneva, Switzerland, 2014.
- WMO: Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project—Report No. 58, 590 pp., Geneva, Switzerland, 2019.
- 20 Wood, S. W., Bodeker, G. E., Boyd, I. S., Jones, N. B., Connor, B. J., Johnston, P. V., Matthews, W. A., Nichol, S. E., Murcray, F. J., Nakajima, H., and Sasano, Y.: Validation of version 5.20 ILAS HNO₃, CH₄, N₂O, O₃, and NO₂ using ground-based measurements at Arrival Heights and Kiruna, *J. Geophys. Res.*, 107, 8208, doi:10.1029/2001JD000581, 2002.
- Wood, S. W., Batchelor, R. L., Goldman, A., Rinsland, C. P., Connor, B. J., Murcray, F. J., Stephen, T. M., and Heuff, D. N.: Ground-based nitric acid measurements at Arrival Heights, Antarctica, using solar and lunar Fourier transform infrared observations, *J. Geophys. Res.*, 109, D18307, doi:10.1029/2004JD004665, 2004.
- 25 Yang, E.-S., Cunnold, D. M., Newchurch, M. J., Salawitch, R. J., McCormick, M. P., Russell III, J. M., Zawodny, J. M., and Oltmans, S. J.: First stage of Antarctic ozone recovery, *J. Geophys. Res.*, 113, D20308, doi:10.1029/2007JD009675, 2008.
- Ziemke, J. R., Chandra, S., Labow, G. J., Bhartia, P. K., Froidevaux, L., and Witte, J. C.: A global climatology of tropospheric and stratospheric ozone derived from Aura OMI and MLS measurements, *Atmos. Chem. Phys.*, 11, 9237-9251, 30 doi:10.5194/acp-11-9237-2011, 2011.

Table 1. FTIR observation dates at Syowa Station in 2007 and 2011

Month	Dates (2007)	Dates (2011)	Number of days inside the polar vortex (2007/2011)	Number of days in the boundary region of the polar vortex (2007/2011)	Number of days outside the polar vortex (2007/2011)	Number of measurement days (2007/2011)
March	25		0/0	0/0	1/0	1/0
April	1, 3, 4, 5, 8, 24, 26, 28		0/0	0/0	8/0	8/0
May	8, 9, 10, 13, 14, 15, 20, 21, 22		7/0	0/0	2/0	9/0
June			0/0	0/0	0/0	0/0
July	29, 30		0/0	2/0	0/0	2/0
August	1, 8, 9, 10, 24, 25, 26, 28, 29		8/0	1/0	0/0	9/0
September	1, 4, 5, 6, 7, 8, 16, 18, 23, 26, 27, 30	25, 29, 30	12/3	0/0	0/0	12/3
October	6, 10, 11, 14, 19, 20, 25, 26, 27	1, 3, 4, 8, 11, 22, 23, 24, 26	9/9	0/0	0/0	9/9
November	2, 3, 5, 6, 7, 8, 9, 10, 11, 16, 17, 18, 19, 21, 27, 29, 30	1, 2, 3, 9, 11, 16, 19	12/7	1/0	4/0	17/7
December	4, 7, 8, 9, 13, 15, 16, 17, 20, 22, 29		8/0	0/0	3/0	11/0
Total			56/19	4/0	18/0	78/19

Table 12. Retrieval parameters of SFIT2

Species	O ₃	HNO ₃	HCl
Spectroscopy	HITRAN 2008	HITRAN 2008	HITRAN 2008
Pressure and temperature profile	Daily sonde (0-30 km)	Daily sonde (0-30 km)	Daily sonde (0-30 km)
	CIRA 86 (30-100 km)	CIRA 86 (30-100 km)	CIRA 86 (30-100 km)
A priori profiles	Monthly averaged by ozonesonde (0-30 km) & ILAS-II (30-100 km)	Monthly averaged by ILAS-II	Monthly averaged by HALOE
Microwindows (cm ⁻¹)	1002.578 – 1003.500	867.000 – 869.591	2727.730 – 2727.830
	1003.900 – 1004.400	872.800 – 874.000	2775.700 – 2775.800
	1004.578 – 1005.000		2925.800 – 2926.000
Retrieved interfering species	O ₃ (668), O ₃ (686), CO ₂ , H ₂ O	H ₂ O, OCS, NH ₃ , CO ₂ , C ₂ H ₆	CO ₂ , H ₂ O, O ₃ , NO ₂
Typical retrieval error (%) for 15-25 km	5	15	17
Typical vertical resolution (km)	7	5	6
Mean degrees of freedoms (DOFS)	4.9	2.8	2.3

Table 23. Summary of validation results of FTIR profiles compared with ozonesonde and Aura/MLS measurements, and possible Aura/MLS biases from literatures

	<u>Number of coincidences</u>	<u>Root mean squares of official errors* (%) at 18-22 km</u>	<u>D (%) at 18-22 km</u>	<u>Min/Max (%) at 18-22 km</u>	<u>Range of mean absolute differences Agreement at 15-25 km (ppmv/ppbv)</u>	<u>Literature values</u>
<u>O₃ (sonde)</u>	<u>14</u>	<u>7.1</u>	<u>+6.1</u>	<u>-10.4/+19.2</u>	<u>-0.02~+0.40</u>	
<u>O₃ (MLS)</u>	<u>33</u>	<u>9.4</u>	<u>-5.5+6.2</u>	<u>-10.46.3/+19.24.5</u>	<u>-0.1302~+0.1640</u>	<u>Aura/MLS is +8% higher than ACE-FTS at 70°S (Froidevoux et al., 2008)</u>
<u>HNO₃</u>	<u>47</u>	<u>19.2</u>	<u>+13.2</u>	<u>+0.2/+21.9</u>	<u>-0.56~+0.57</u>	<u>Aura/MLS no bias with errors (0.6 ppbv) (Livesey et al., 2011)</u>
<u>HCl</u>	<u>50</u>	<u>39.5</u>	<u>-9.7</u>	<u>-14.6/-3.0</u>	<u>-0.20~+0.09</u>	<u>Aura/MLS > HALOE by 10-15%, precision 0.2-0.6 ppbv (Livesey et al., 2013)</u>

*Root mean squares of official absolute and relative errors given by each data set.

Table A1. FTIR observation dates at Syowa Station in 2007 and 2011

<u>Month</u>	<u>Dates</u> <u>(2007)</u>	<u>Dates</u> <u>(2011)</u>	<u>Number of days</u> <u>inside the polar</u> <u>vortex</u> <u>(2007/2011)</u>	<u>Number of days</u> <u>in the boundary</u> <u>region of the</u> <u>polar vortex</u> <u>(2007/2011)</u>	<u>Number of days</u> <u>outside the polar</u> <u>vortex</u> <u>(2007/2011)</u>	<u>Number of</u> <u>measurement</u> <u>days</u> <u>(2007/2011)</u>
<u>March</u>	<u>25</u>		<u>0 / 0</u>	<u>0 / 0</u>	<u>1 / 0</u>	<u>1 / 0</u>
<u>April</u>	<u>1, 3, 4, 5, 8, 24, 26, 28</u>		<u>0 / 0</u>	<u>0 / 0</u>	<u>8 / 0</u>	<u>8 / 0</u>
<u>May</u>	<u>8, 9, 10, 13, 14, 15, 20, 21, 22</u>		<u>7 / 0</u>	<u>0 / 0</u>	<u>2 / 0</u>	<u>9 / 0</u>
<u>June</u>			<u>0 / 0</u>	<u>0 / 0</u>	<u>0 / 0</u>	<u>0 / 0</u>
<u>July</u>	<u>29, 30</u>		<u>0 / 0</u>	<u>2 / 0</u>	<u>0 / 0</u>	<u>2 / 0</u>
<u>August</u>	<u>1, 8, 9, 10, 24, 25, 26, 28, 29</u>		<u>8 / 0</u>	<u>1 / 0</u>	<u>0 / 0</u>	<u>9 / 0</u>
<u>September</u>	<u>1, 4, 5, 6, 7, 8, 16, 18, 23, 26,</u> <u>27, 30</u>	<u>25, 29, 30</u>	<u>12 / 3</u>	<u>0 / 0</u>	<u>0 / 0</u>	<u>12 / 3</u>
<u>October</u>	<u>6, 10, 11, 14, 19, 20, 25, 26, 27</u>	<u>1, 3, 4, 8, 11, 22, 23,</u> <u>24, 26</u>	<u>9 / 9</u>	<u>0 / 0</u>	<u>0 / 0</u>	<u>9 / 9</u>
<u>November</u>	<u>2, 3, 5, 6, 7, 8, 9, 10, 11, 16,</u> <u>17, 18, 19, 21, 27, 29, 30</u>	<u>1, 2, 3, 9, 11, 16, 19</u>	<u>12 / 7</u>	<u>1 / 0</u>	<u>4 / 0</u>	<u>17 / 7</u>
<u>December</u>	<u>4, 7, 8, 9, 13, 15, 16, 17, 20,</u> <u>22, 29</u>		<u>8 / 0</u>	<u>0 / 0</u>	<u>3 / 0</u>	<u>11 / 0</u>
<u>Total</u>			<u>56 / 19</u>	<u>4 / 0</u>	<u>18 / 0</u>	<u>78 / 19</u>

Table 4. Summary of minor atmospheric species variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
CIO-enhanced-period (day)	230-260	230-260	220-240	230-250
Variation when CIO-enhanced (ppbv)	0-1.3	0-1.5	0-2.2	0-2.2
HCl-value before winter (ppbv)	1.5-1.8	1.2-1.6	2.1-2.4	1.8-2.2
HCl-starting-ending-day-of-decrease (day)	140-180	140-180	130-180	140-170
Variation when HCl~0 (ppbv)	0-0.3	0-0.3	0.1-1.0	0.1-0.9
HCl-starting-ending-day-of-increase (day)	250-300	250-300	240-280	240-300
HCl-Value-after-increase (ppbv)	2.6-3.0	2.5-2.8	2.1-2.4	2.0-2.5
HCl-Value-outside-polar-vortex (ppbv)	1.5-2.0	1.0-1.8	1.5-2.0	1.5-2.0
CIONO ₂ -Value-before-winter (ppbv)	~0.5	~0.4	0.6-0.9	0.6-0.7
Variation when CIONO ₂ ~0 (ppbv)	0-1.5	0-1.5	0-2.0	0-2.0
Day-of-CIONO ₂ -enhancement	-	270-300	270-280	270-280
Value-of-CIONO ₂ -enhancement (ppbv)	-	1.5	1.5	1.5
CIONO ₂ -value-after-enhancement (ppbv)	0-0.3	0-0.2	0.8-1.3	0.8-1.1
CIONO ₂ -value-outside-polar-vortex (ppbv)	0.3-0.4	0.2-0.3	0.5-0.7	0.6-0.8
O ₂ -value-before-winter (ppmv)	2.5	2.5	4.0	4.0
O ₂ -starting-ending-day-of-decrease (day)	190-280	200-270	170-260	170-270
O ₂ -minimum-value (ppmv)	0.3	0.5	2.0	1.0
O ₂ -value-after-recovery (ppmv)	0.8	0.8	2.4-4.0	2.0-3.5
HNO ₂ -value-before-winter (ppbv)	6-10	8-10	15-16	13-15
HNO ₂ -starting-ending-day-of-decrease (day)	160-190	150-180	140-180	150-180
HNO ₂ -minimum-value (ppbv)	0	0	2	1
HNO ₂ -value-after-recovery (ppbv)	3-4	3-4	4-6	4-5

* ‘CIO-enhanced-period’ is defined as the period when CIO-values were more than 80 % of its maximum value.

Figures

Figure 1. Averaging kernel functions of the SFIT2 retrievals for (a) O_3 , (b) HNO_3 , and (c) HCl .

- 5 Figure 2. (a) Mean absolute and (b) mean relative differences of O_3 profiles retrieved from FTIR measurements minus those from ozonesonde measurements. Horizontal bars indicate the standard deviation of differences at each altitude. (c) Mean absolute and (d) mean relative differences of O_3 profiles retrieved from FTIR measurements minus those from Aura/MLS measurements. (e) Mean absolute and (f) mean relative differences of HNO_3 profiles retrieved from FTIR measurements minus those from Aura/MLS measurements. (g) Mean absolute and (h) mean relative differences of HCl profiles retrieved from FTIR measurements minus those from Aura/MLS measurements. Horizontal bars indicate the root mean squares standard deviation of differences at each altitude. Horizontal dashed bars indicate the altitude range of our focus (15-25 km).
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- Figure 3. Time series of (a) daytime hour temperatures at 18 km in (b) 2007 and (c) 2011, and at 22 km in (d) 2007 and (e) 2011 over Syowa Station using ERA-Interim data. Approximate saturation temperatures for nitric acid trihydrate PSC (T_{NAT}) and ice PSC (T_{ICE}) calculated by assuming 6 ppbv HNO_3 and 4.5 ppmv H_2O are also plotted in the figures by dotted lines. Dates when PSCs were observed over Syowa Station are indicated by asterisks on the bottom of the figures.
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- Figure 4. Time series of (a) HCl , ClONO_2 , ClO , Cl_y^* , (b) O_3 , and HNO_3 mixing ratios at 18 km in 2007 over Syowa Station. $\text{O}_3(\text{FTIR})$, $\text{HCl}(\text{FTIR})$, and $\text{HNO}_3(\text{FTIR})$ were measured by FTIR at Syowa Station, while $\text{HCl}(\text{MLS})$, $\text{ClO}(\text{MLS})$, and $\text{HNO}_3(\text{MLS})$ were measured by Aura/MLS. $\text{O}_3(\text{sonde})$ was measured by ozonesonde. ClONO_2 was measured by Envisat/MIPAS. Cl_y^* is calculated from Aura/MLS N_2O value. See text in detail. The unit of O_3 is ppmv and the other gases are ppbv. The dark shaded area, the light shaded area, and the white area indicate the days when Syowa Station was located outside, in the boundary region, and inside the polar vortex, respectively.
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Figure 5. Same as Figure 4 but in 2011.

Figure 6. Same as Figure 4 but at 22 km.

- 30 Figure 7. Same as Figure 5 but at 22 km.

Figure 8. Time series of the ratios of HCl (dark blue or light blue), ClONO_2 (yellow), and ClO (red), and $\text{Cl}_y^* (= \text{HCl} + \text{ClONO}_2 + \text{ClO})$ to total chlorine (Cl_y^*) over Syowa Station at 18 km in (a) 2007 and in (b) 2011. Light blue shows

either ClONO₂ or ClO data was missing on that day, while dark blue shows all three data were available on that day. Shaded areas are the same as Figure 4.

Figure 9. Same as Figure 8 but at 22 km.

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Figure 10. Scatter plot between ClO (Aura/MLS) and ClONO₂ (Envisat/MIPAS) mixing ratios between August 8 and September 17 (day 220 – 260) at 18 km and 22 km in 2007 and 2011. Crosses, triangles, and squares represent the data when Syowa Station was located inside the polar vortex, the boundary region, and outside the polar vortex, respectively. Solid lines are regression lines obtained by RMA-~~(Reduced Major Axis)~~ regression. Color represents the equivalent latitude over Syowa Station on that day. Circles with crosses represent the days which are shown in Figures 13 and 14.

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Figure 11. Daily time series of measured and modeled minor species over Syowa Station at 18 km. Black diamonds are data by FTIR, red squares are by Aura/MLS and Envisat/MIPAS, blue triangles are data by MIROC3.2 CCM. (a) is for ClO, (b) is for HCl, (c) is for ClONO₂, (d) is for Cly, and (e) is for O₃ in 2007. (f) is for ClO, (g) is for HCl, (h) is for ClONO₂, (i) is for Cly, and (j) is for O₃ in 2011.

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Figure 12. Same as Figure 11 but for 22 km.

Figure 13. Polar southern hemispheric plots for ERA-Interim temperature, simulated mixing ratios of O₃, NO₂, HNO₃, ClO, HCl, and ClONO₂ by a MIROC3.2 chemistry-climate model (CCM) at 50 hPa for June 24 (day 175), September 2 (day 245), September 6 (day 249), and October 6 (day 279), 2007. Polar vortex ~~boundary edges defined as the method described in Appendix B~~ at ~~45075 K-calculated from ERA-Interim reanalysis data~~ was plotted by ~~whitedotted~~ circle in each panel. The location of Syowa Station ~~wa~~is shown by white star in each panel.

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Figure 14. Same as Figure 13 but for July 5 (day 186), August 19 (day 231), August 21 (day 233), and October 9 (day 282), 2011. Polar vortex edges on July 5 plotted by dotted while circles indicate that the inner vortex edge was defined on this day.

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Figure 15. Three-hourly zonal-mean time series of MIROC3.2 CCM outputs for (a) ClO+2*Cl₂O₂+2*Cl₂, (b) Cl₂O₂, (c) Cl₂, (d) ClO, (e) HOCl, (f) HCl, and (g) ClONO₂ during day number 120–300 at 50 hPa in 2007.

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Figure A1. Time-equivalent latitude sections of MPV (contours) and its gradient with respect to EL (colors) at (a) 450 K and (b) 560 K isentropic PT surfaces in 2007. Black dots represent the inner and outer edge(s) of the polar vortex. Red dots represent the EL of Syowa Station on each day.

Figure A2. Same as Figure A1 but for the year in 2011.

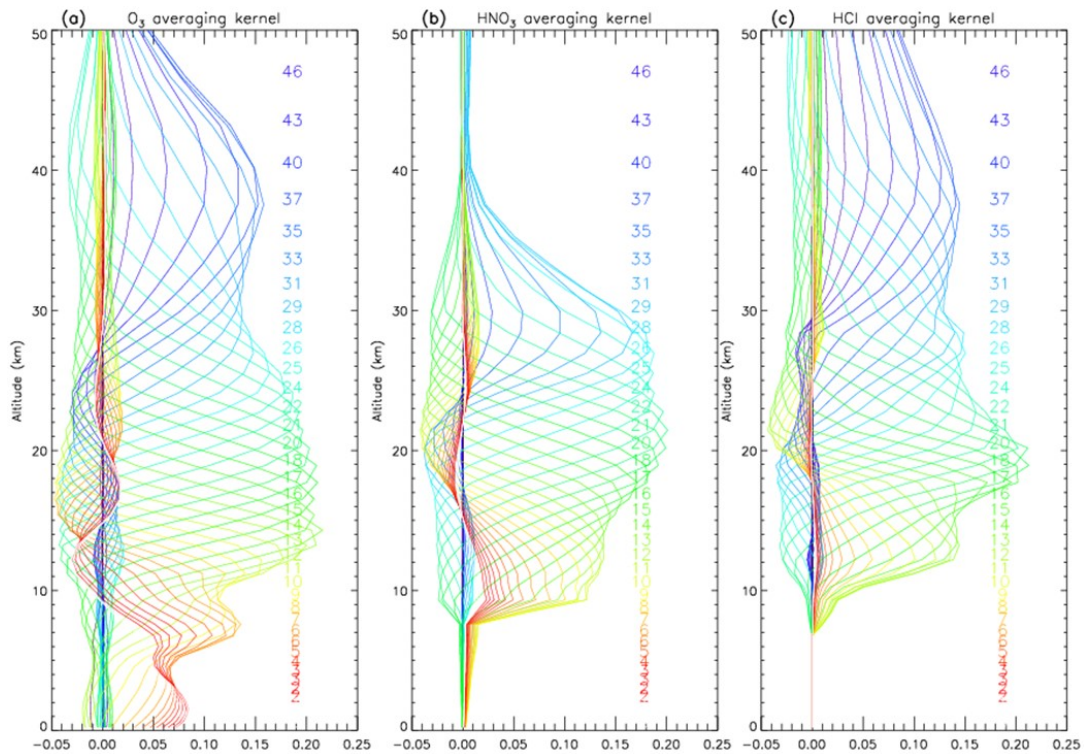


Figure 1. Averaging kernel functions of the SFIT2 retrievals for (a) O_3 , (b) HNO_3 , and (c) HCl .

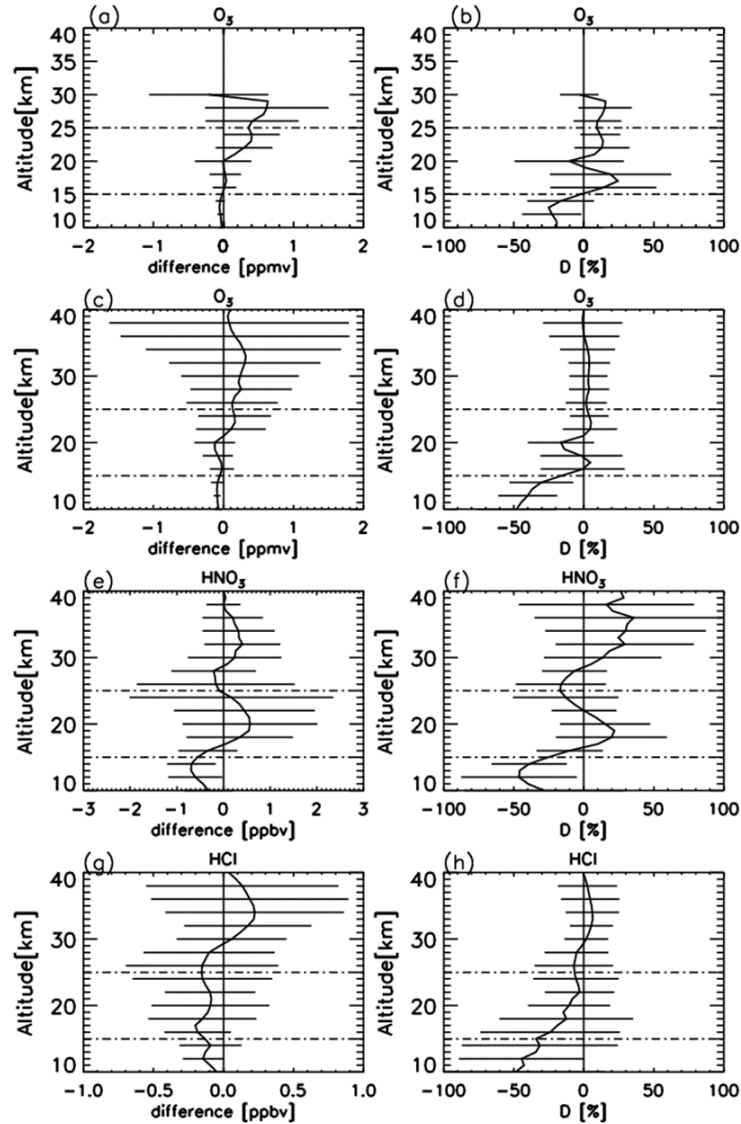


Figure 2. (a) Mean absolute and (b) mean relative differences of O_3 profiles retrieved from FTIR measurements minus those from ozonesonde measurements. (c) Mean absolute and (d) mean relative differences of O_3 profiles retrieved from FTIR measurements minus those from Aura/MLS measurements. (e) Mean absolute and (f) mean relative differences of HNO_3 profiles retrieved from FTIR measurements minus those from Aura/MLS measurements. (g) Mean absolute and (h) mean relative differences of HCl profiles retrieved from FTIR measurements minus those from Aura/MLS measurements. Horizontal bars indicate the root mean squares of differences at each altitude. Horizontal dashed bars indicate the altitude range of our focus (15-25 km).

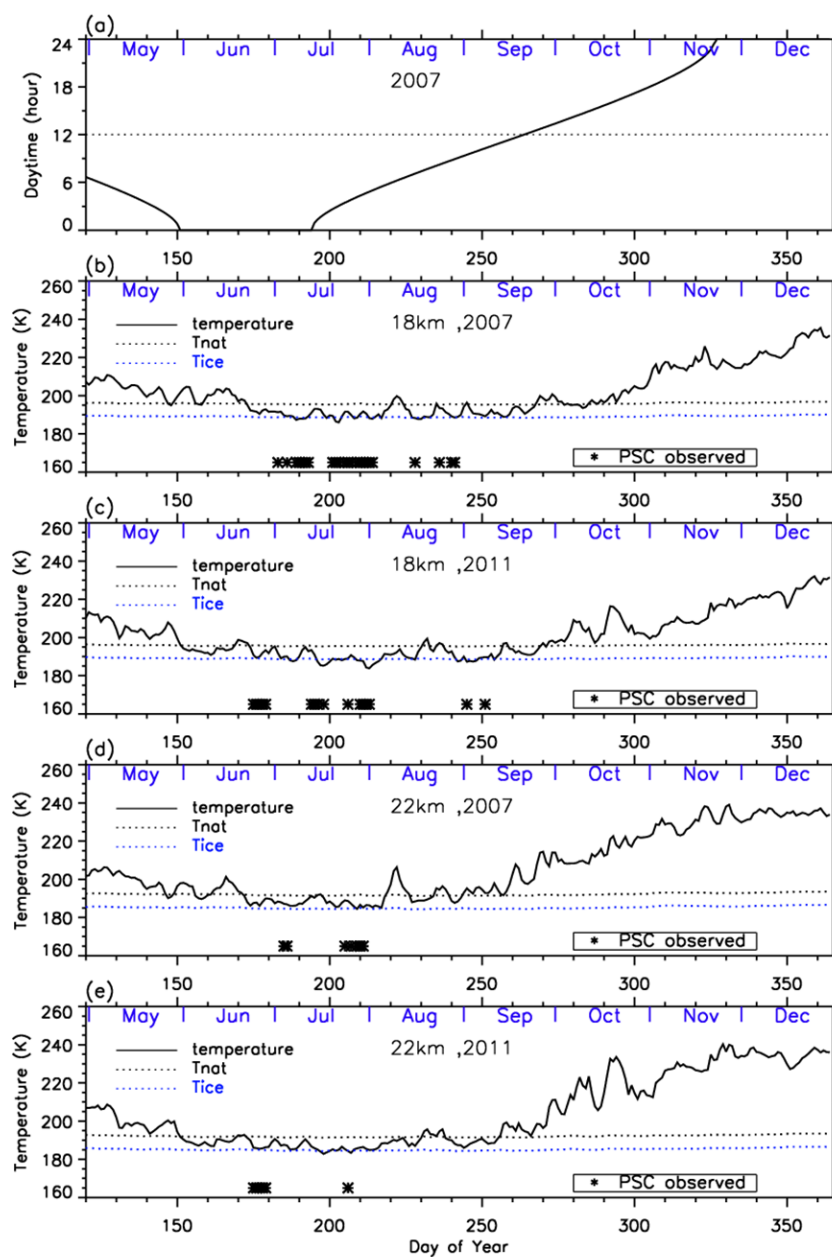


Figure 3. Time series of (a) daytime hour, temperatures at 18 km in (b) 2007 and (c) 2011, and at 22 km in (d) 2007 and (e) 2011 over Syowa Station using ERA-Interim data. Approximate saturation temperatures for nitric acid trihydrate PSC (T_{NAT}) and ice PSC (T_{ICE}) calculated by assuming 6 ppbv HNO_3 and 4.5 ppmv H_2O are also plotted in the figures by dotted lines. Dates when PSCs were observed over Syowa Station are indicated by asterisks on the bottom of the figures.

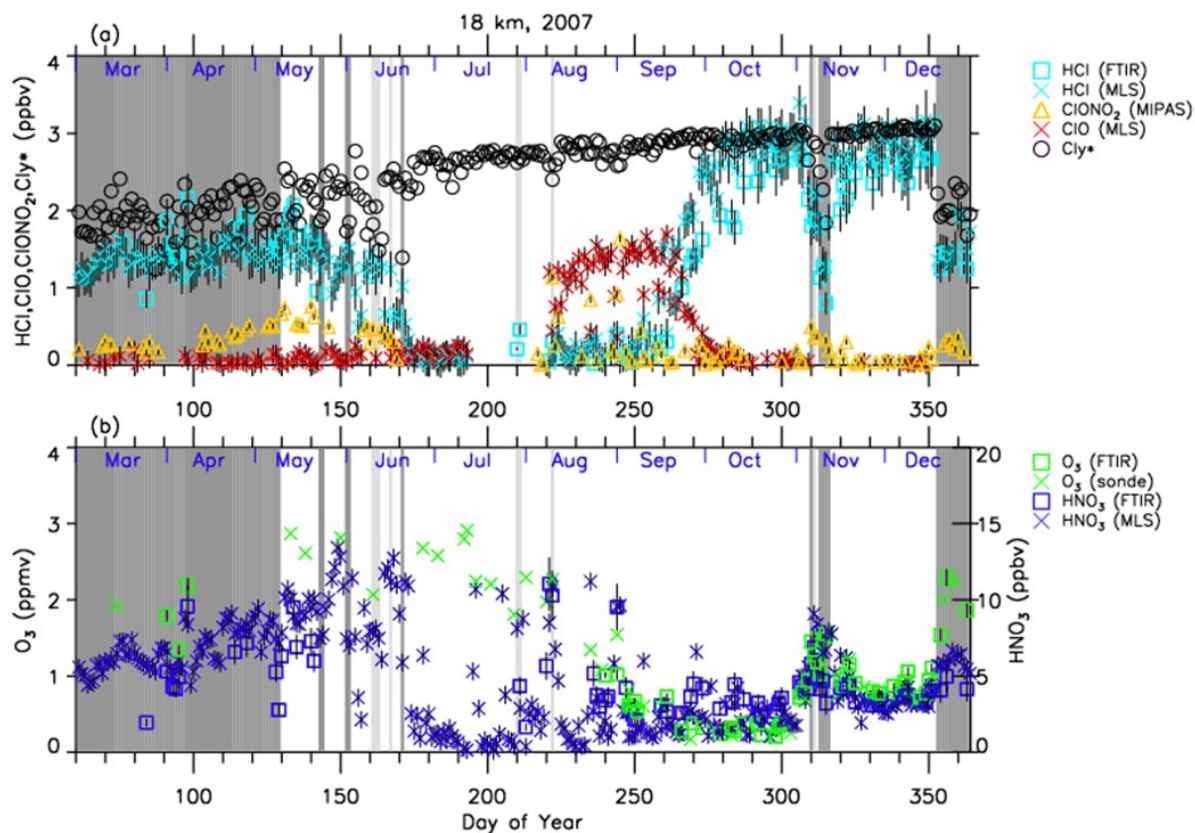


Figure 4. Time series of (a) HCl, ClONO₂, ClO, Cl_y*, (b) O₃, and HNO₃ mixing ratios at 18 km in 2007 over Syowa Station. O₃(FTIR), HCl(FTIR), and HNO₃(FTIR) were measured by FTIR at Syowa Station, while HCl(MLS), ClO(MLS), and HNO₃(MLS) were measured by Aura/MLS. O₃(sonde) was measured by ozonesonde. ClONO₂ was measured by Envisat/MIPAS. Cl_y* is calculated from Aura/MLS N₂O value. See text in detail. The unit of O₃ is ppmv and the other gases are ppbv. The dark shaded area, the light shaded area, and the white area indicate the days when Syowa Station was located outside, in the boundary region, and inside the polar vortex, respectively.

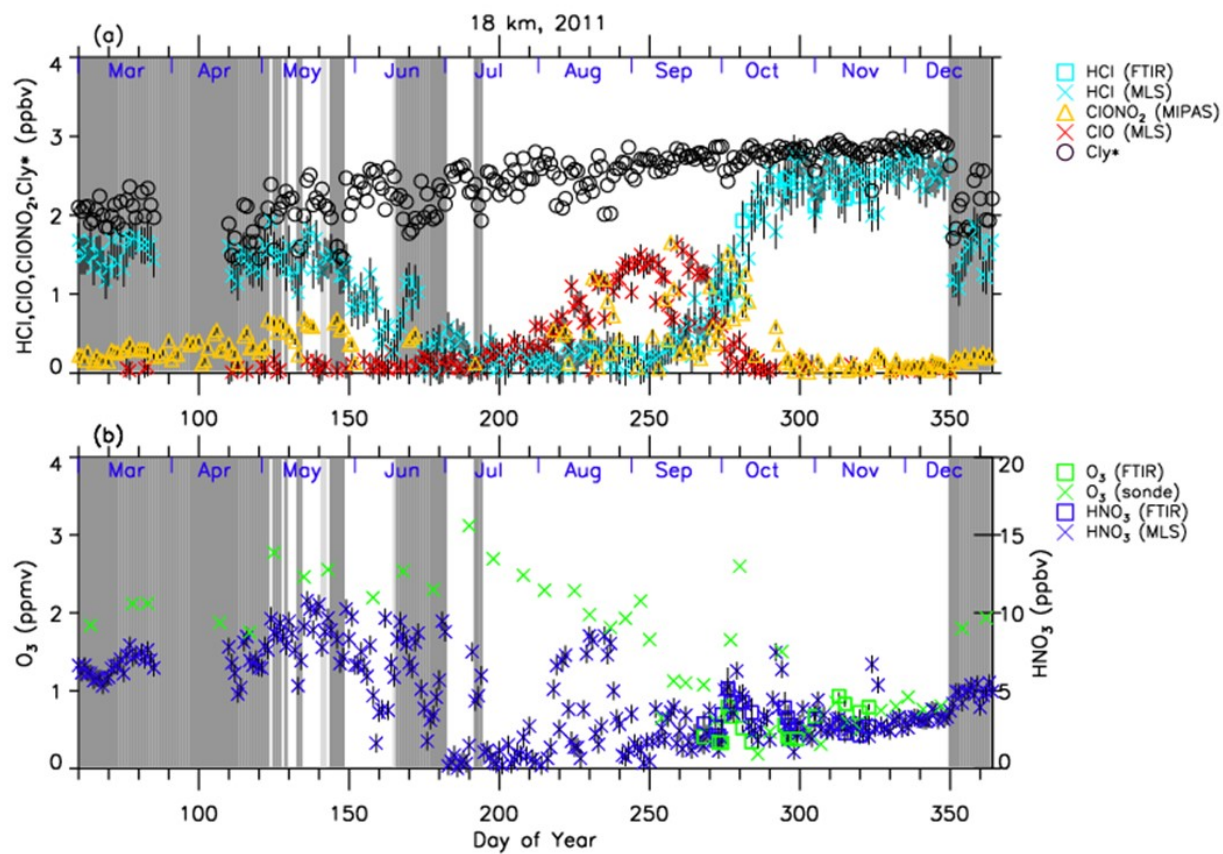


Figure 5. Same as Figure 4 but in 2011.

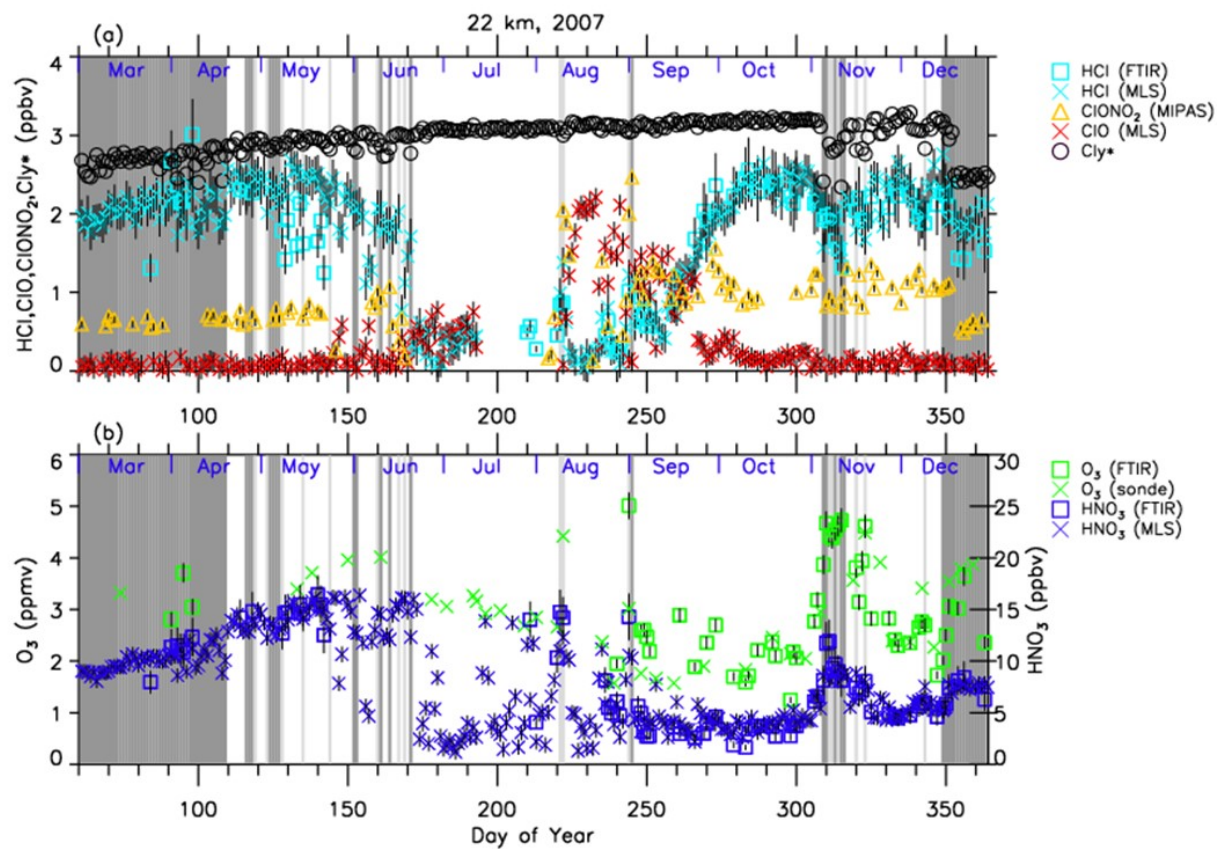


Figure 6. Same as Figure 4 but at 22 km.

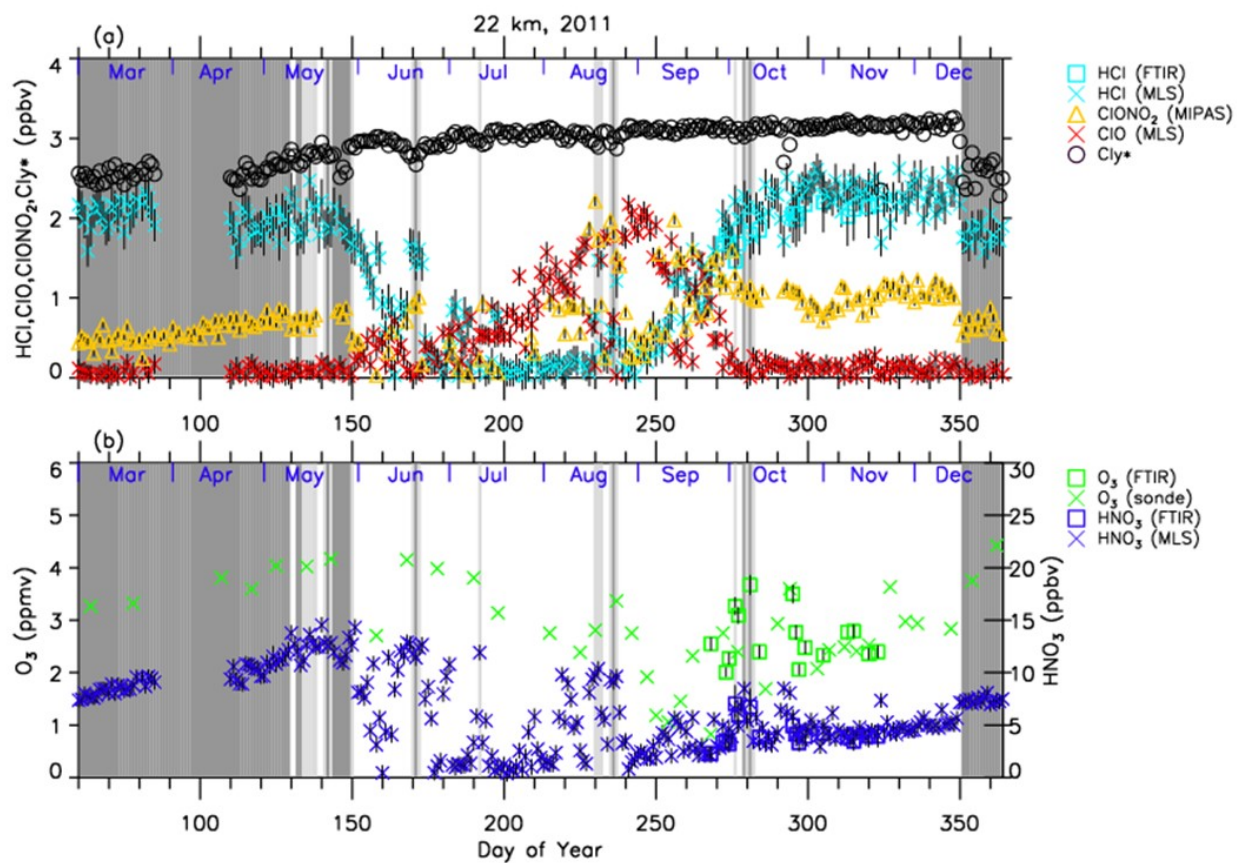


Figure 7. Same as Figure 5 but at 22 km.

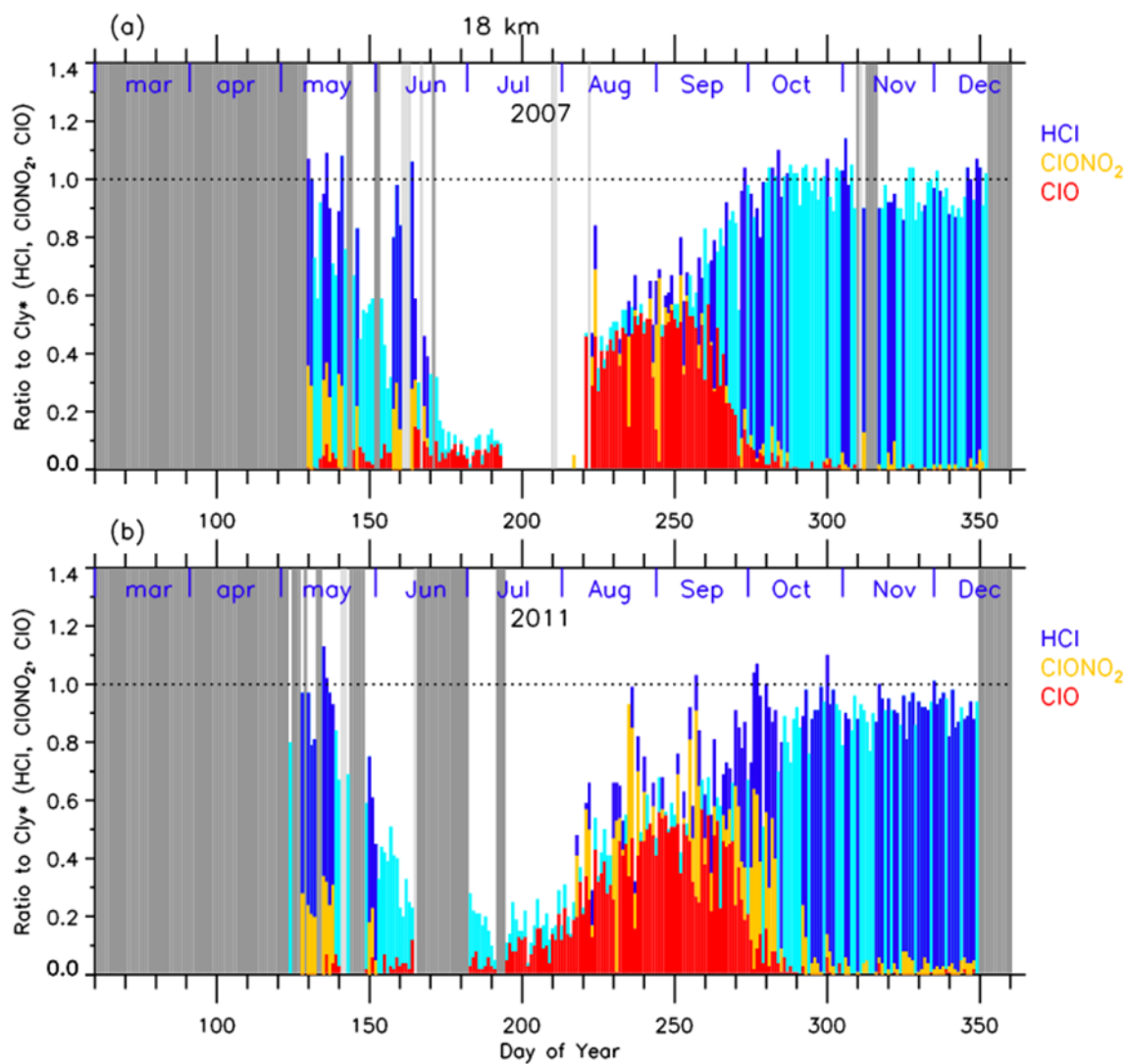


Figure 8. Time series of the ratios of HCl (dark blue or light blue), ClONO_2 (yellow), and ClO (red) to total chlorine (Cl_y^*) over Syowa Station at 18 km in (a) 2007 and in (b) 2011. Light blue shows either ClONO_2 or ClO data was missing on that day, while dark blue shows all three data were available on that day. Shaded areas are the same as Figure 4.

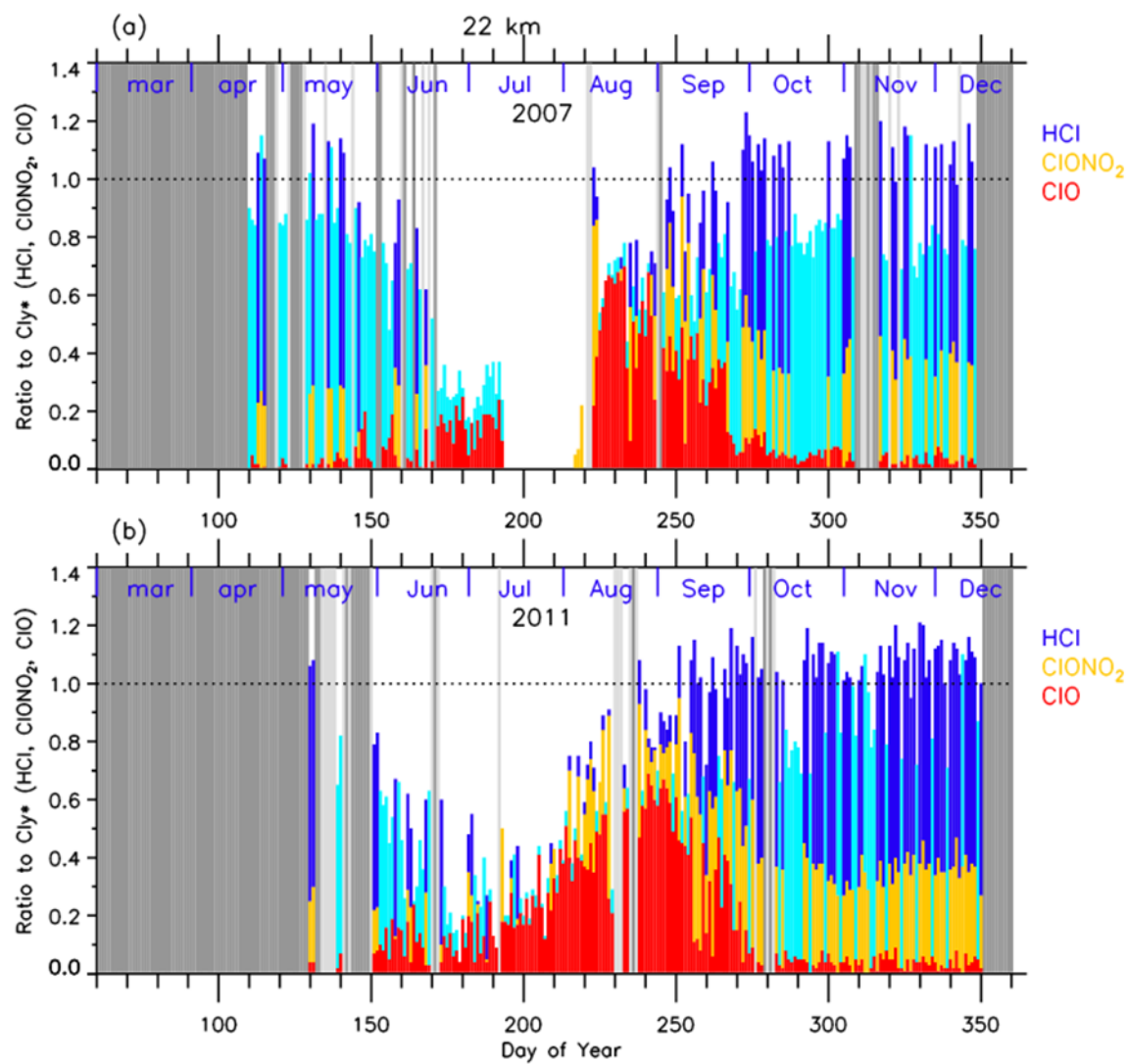


Figure 9. Same as Figure 8 but at 22 km.

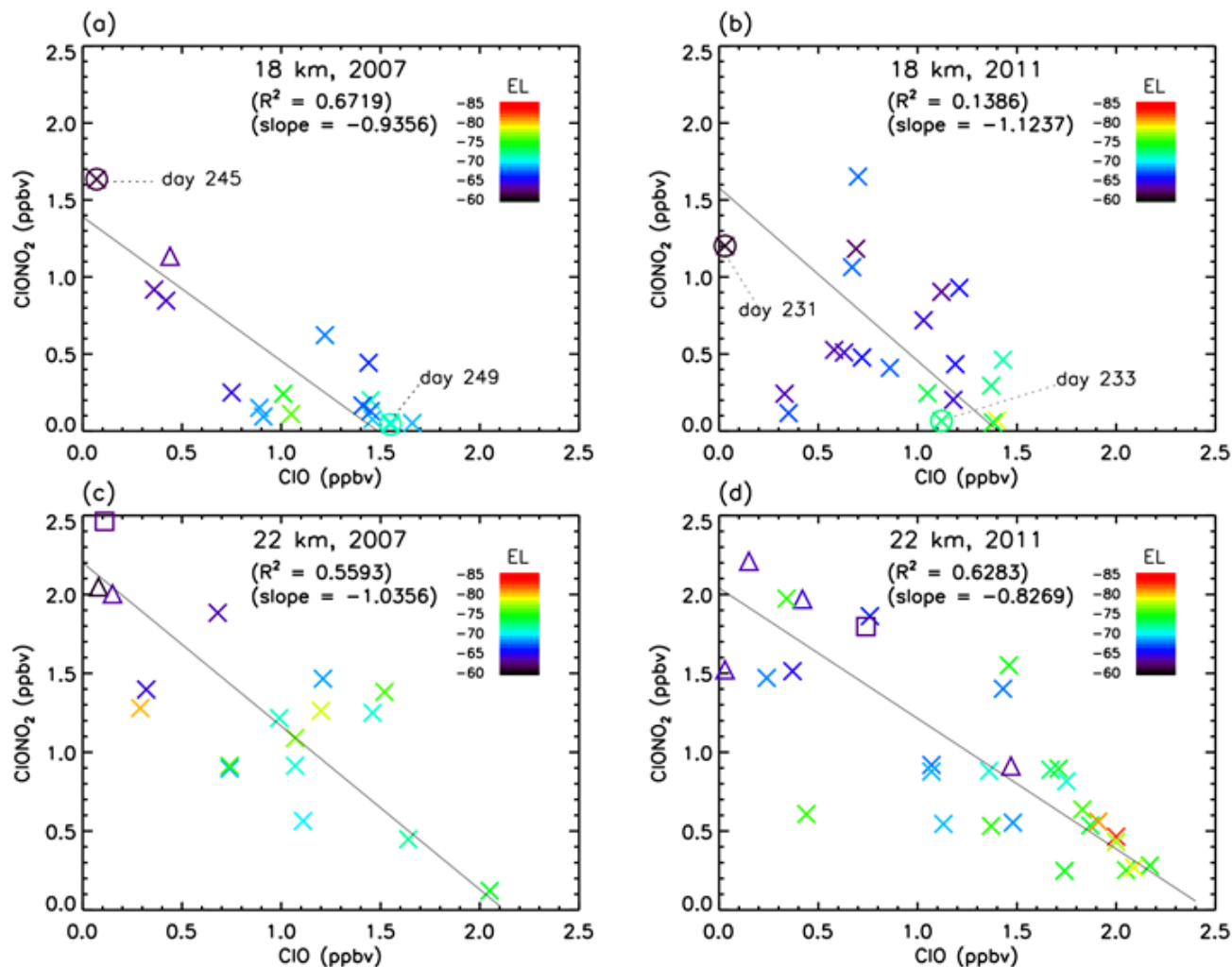


Figure 10. Scatter plot between CIO (Aura/MLS) and ClONO₂ (Envisat/MIPAS) mixing ratios between August 8 and September 17 (day 220 – 260) at 18 km and 22 km in 2007 and 2011. Crosses, triangles, and squares represent the data when Syowa Station was located inside the polar vortex, the boundary region, and outside the polar vortex, respectively. Solid lines are regression lines obtained by RMA regression. Color represents the equivalent latitude over Syowa Station on that day.

30 Circles with crosses represent the days which are shown in Figures 13 and 14.

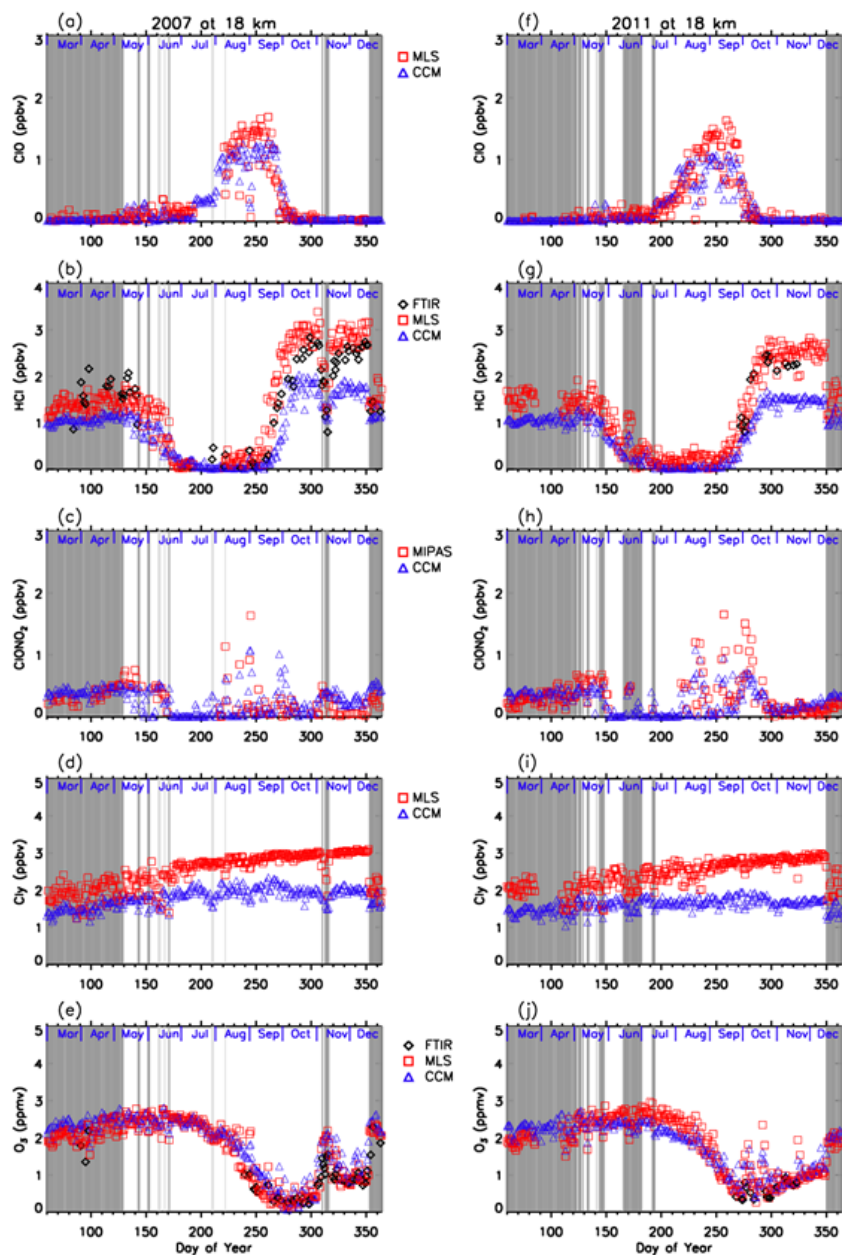


Figure 11. Daily time series of measured and modeled minor species over Syowa Station at 18 km. Black diamonds are data by FTIR, red squares are by Aura/MLS and Envisat/MIPAS, blue triangles are data by MIROC3.2 CCM. (a) is for ClO, (b) is for HCl, (c) is for ClONO₂, (d) is for Cly, and (e) is for O₃ in 2007. (f) is for ClO, (g) is for HCl, (h) is for ClONO₂, (i) is for Cly, and (j) is for O₃ in 2011.

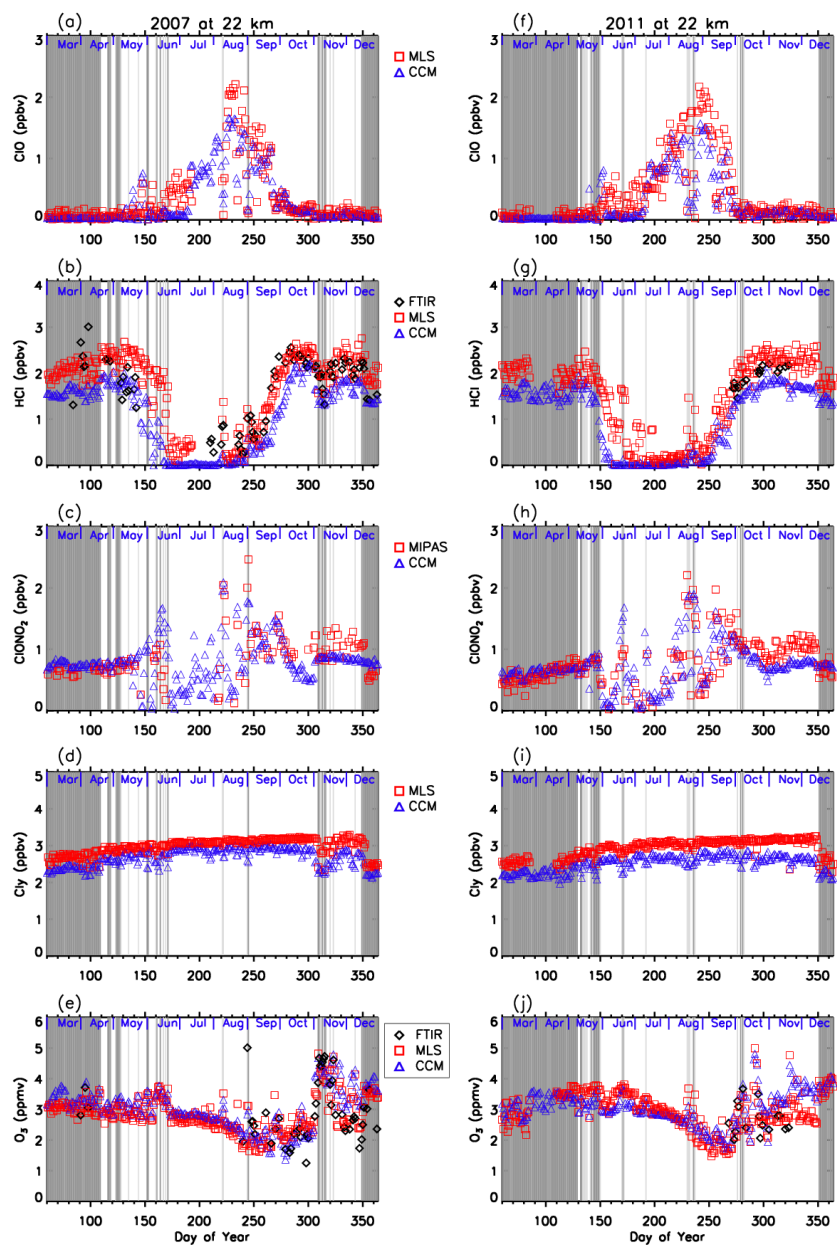


Figure 12. Same as Figure 11 but for 22 km.

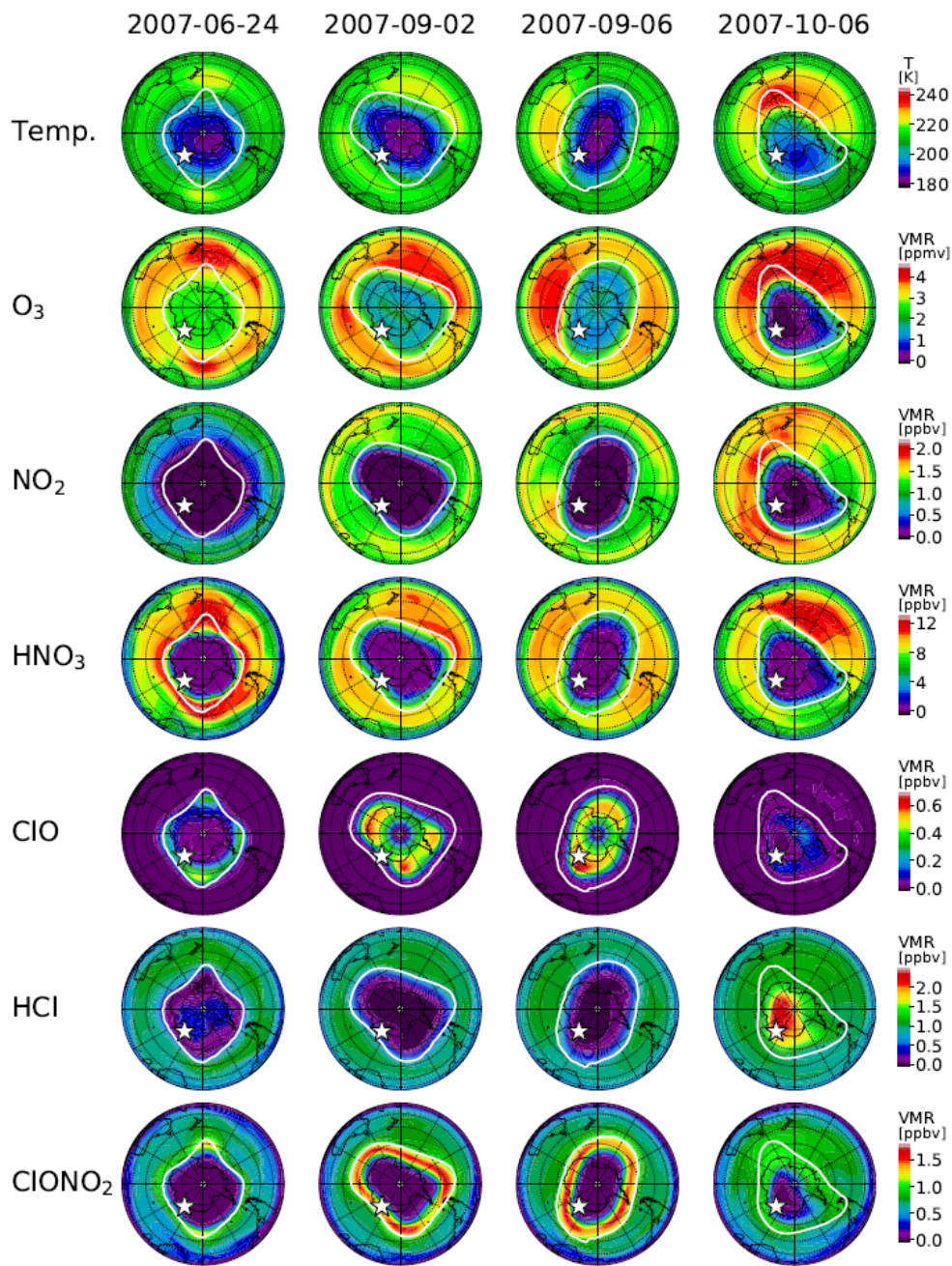


Figure 13. Polar southern hemispheric plots for temperature from the model nudged toward the ERA-Interim data, simulated mixing ratios of O_3 , NO_2 , HNO_3 , ClO , HCl , and $ClONO_2$ by a MIROC3.2 chemistry-climate model (CCM) at 50 hPa for June 24 (day 175), September 2 (day 245), September 6 (day 249), and October 6 (day 279), 2007. Polar vortex edges defined by the method described in Appendix B at 450 K were plotted by white circles in each panel. The location of Syowa Station was shown by white star in each panel.

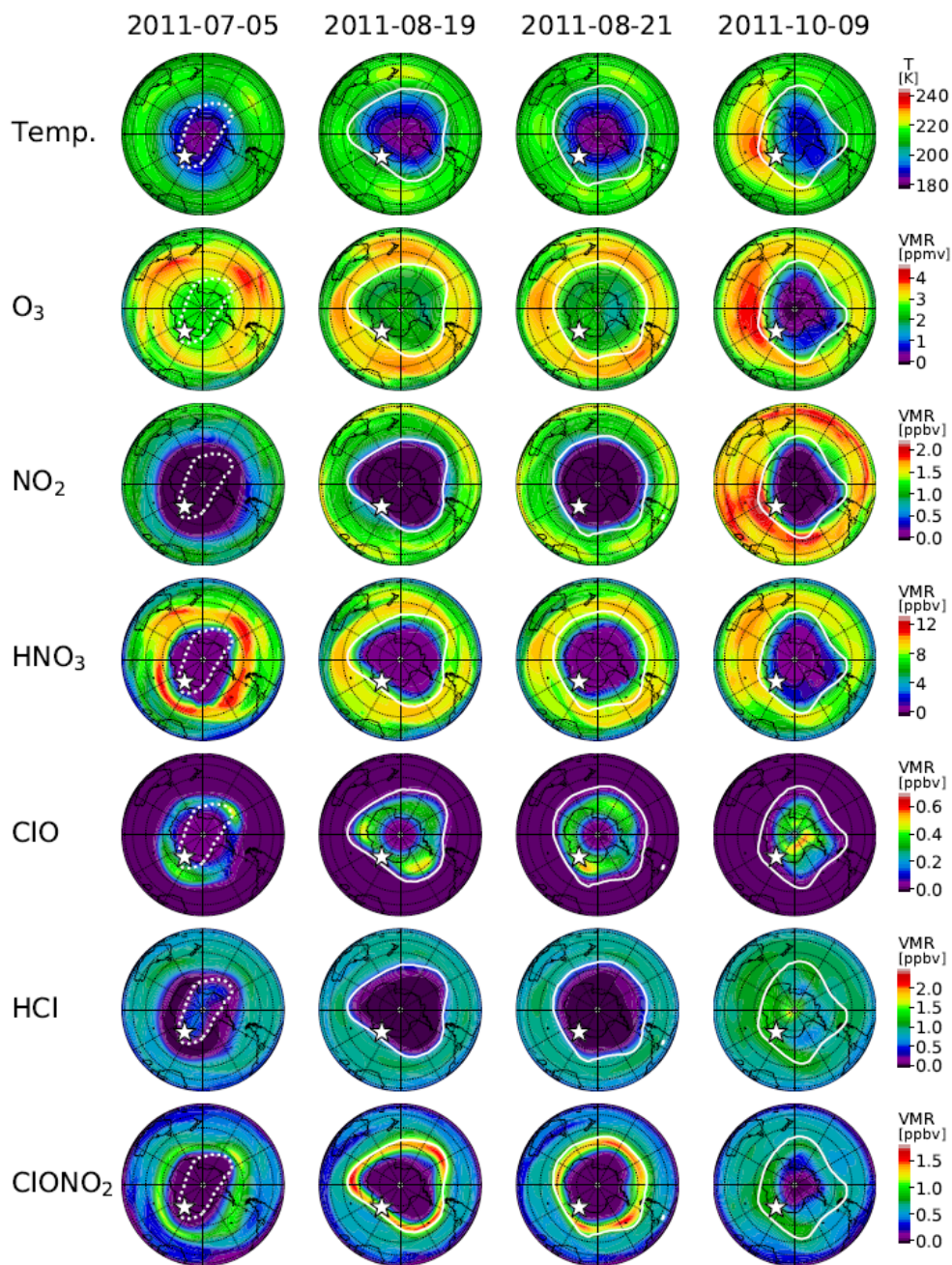


Figure 14. Same as Figure 13 but for July 5 (day 186), August 19 (day 231), August 21 (day 233), and October 9 (day 282), 2011. Polar vortex edges on July 5 plotted by dotted while circles indicate that the inner vortex edge was defined on this day.

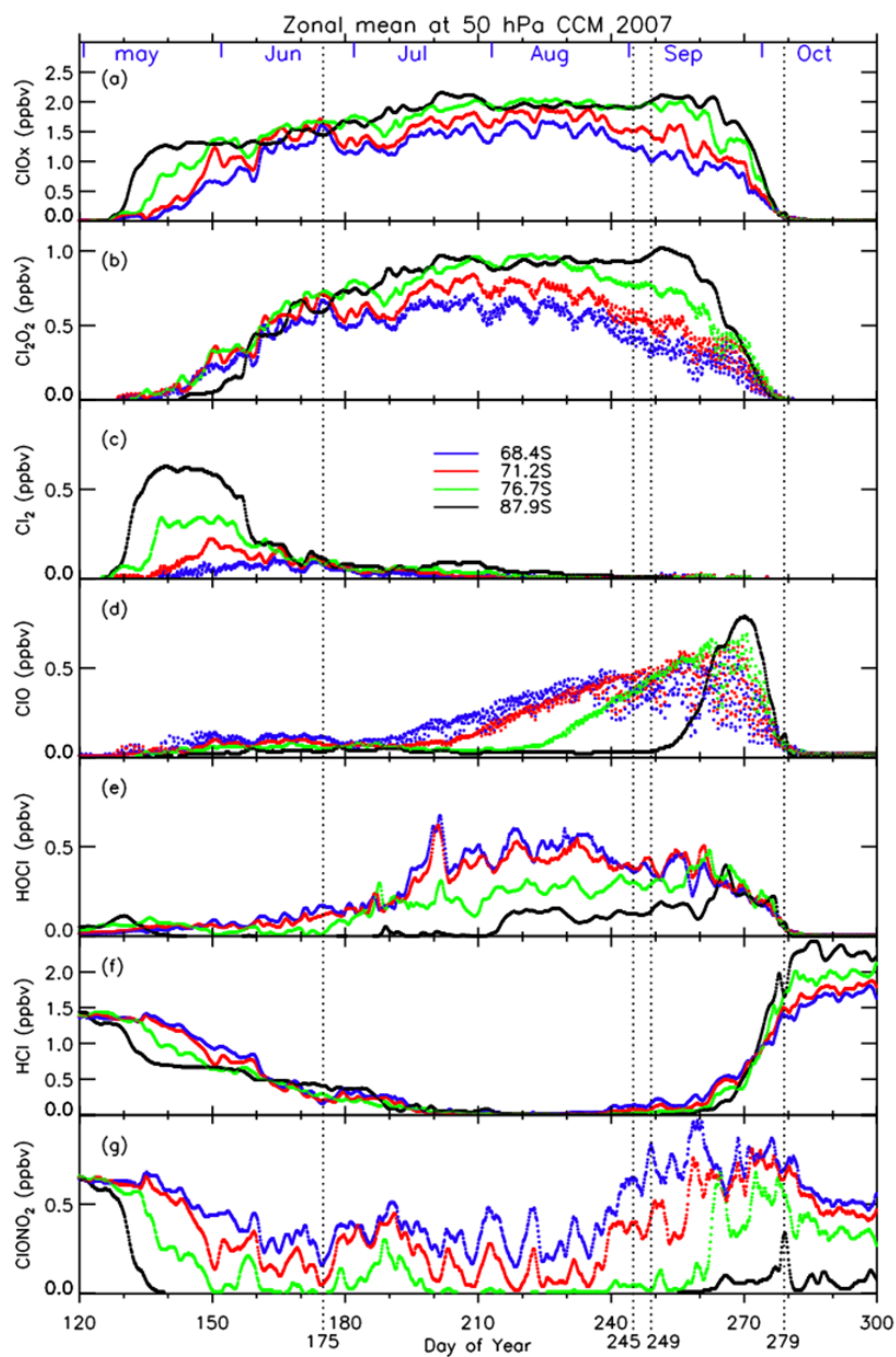


Figure 15. Three-hourly zonal-mean time series of MIROC3.2 CCM outputs for (a) $\text{ClO} + 2 \times \text{Cl}_2\text{O}_2 + 2 \times \text{Cl}_2$, (b) Cl_2O_2 , (c) Cl_2 , (d) ClO , (e) HOCl , (f) HCl , and (g) ClONO_2 during day number 120–300 at 50 hPa in 2007.

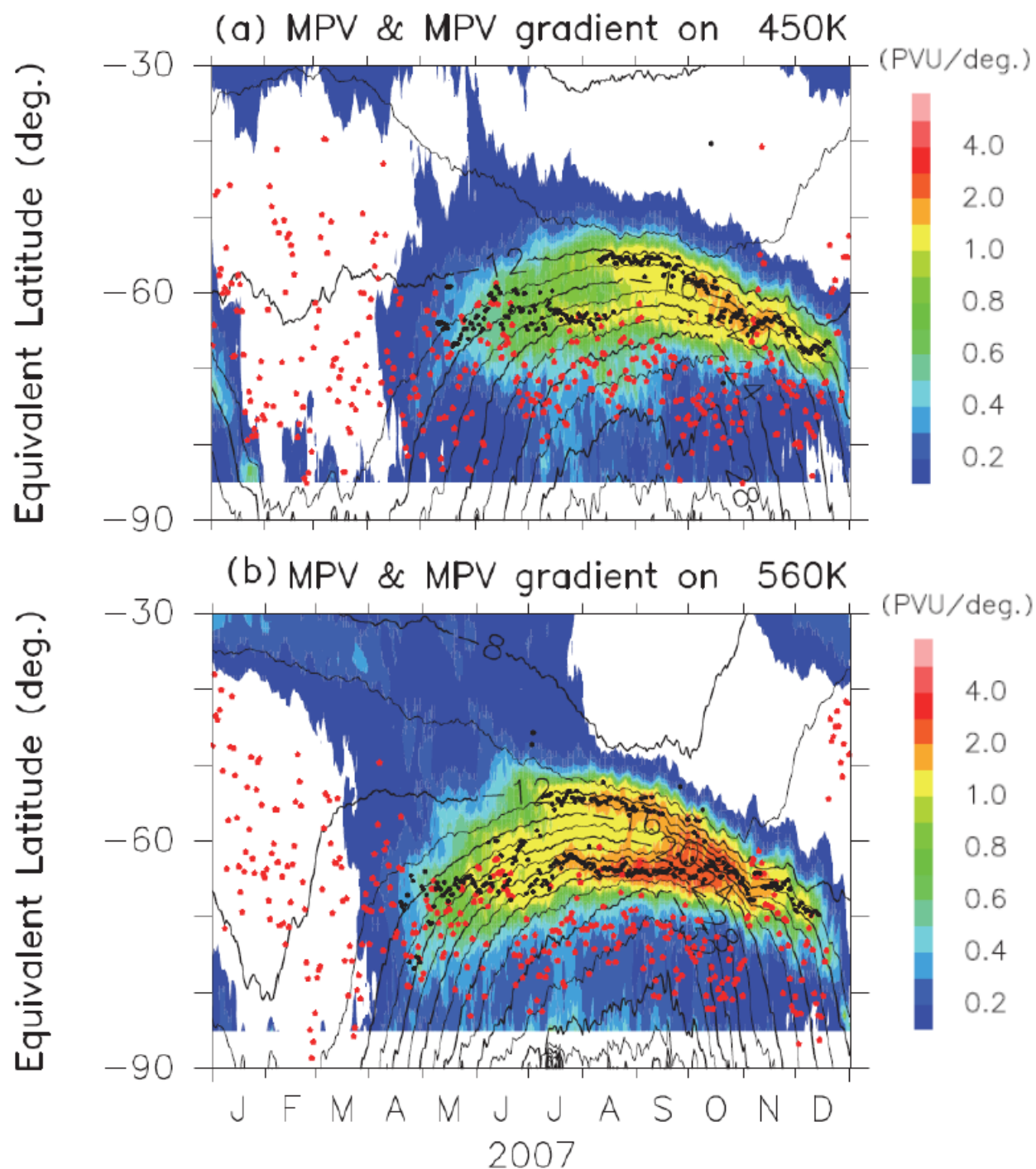


Figure A1. Time-equivalent latitude sections of MPV (contours) and its gradient with respect to EL (colors) at (a) 450 K and (b) 560 K isentropic PT surfaces in 2007. Black dots represent the inner and outer edge(s) of the polar vortex. Red dots represent the EL of Syowa Station on each day.

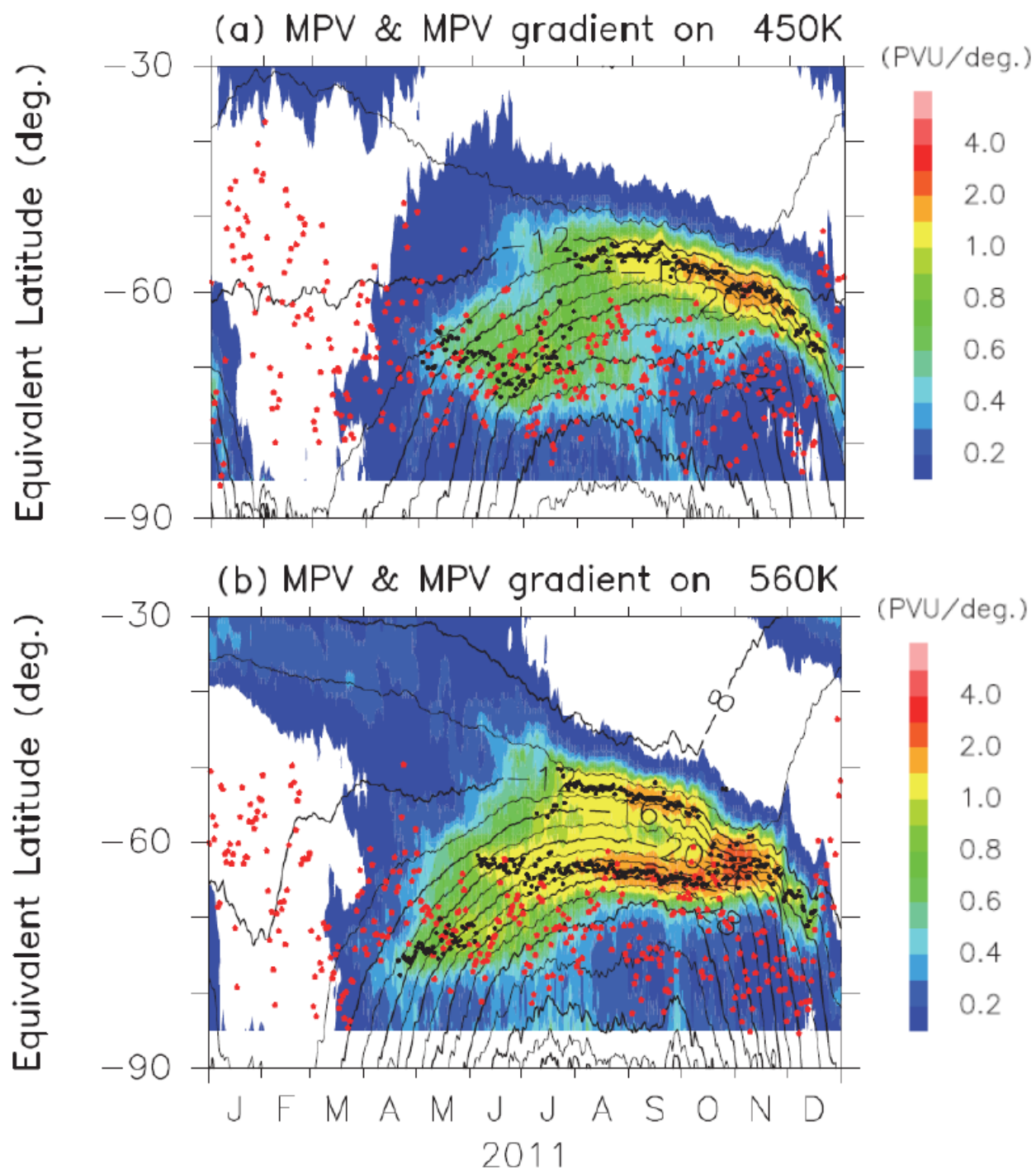


Figure A2. Same as Figure A1 but for the year in 2011.