

Comments to the revised version

We thank the two reviewers for their comments that helped us to improve the paper. We addressed the points and changes made to the revised manuscript in the separate “Reply to Reviewers #1 and #2” which are posted in the interactive discussion.

- 5 For clarity, we here include a version of the paper in which the additions and changes to the previous ACPD manuscript are marked by colored letters. Red-colored changes are mainly for the comments by Reviewer-#1, and blue-colored changes are for those by Reviewer-#2.

Temporal evolution of chlorine and minor species related to ozone depletion ~~observed with ground-based FTIR~~ at Syowa Station, Antarctica ~~and satellites~~ during austral fall to spring in 2007 and 2011

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Abstract.

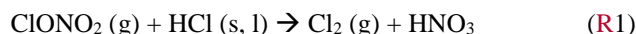
To understand and project future ozone recovery, understanding of the mechanisms related to polar ozone destruction is
15 crucial. For polar stratospheric ozone destruction, chlorine species play an important role, but detailed temporal evolution of
chlorine species in the Antarctic winter is not well understood. 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 related to the ozone hole from the ground in Antarctica. We analyzed temporal
20 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. When the stratospheric temperature over Syowa Station fell
below polar stratospheric cloud (PSC) ~~existencesaturation~~ temperature in early winter, PSCs started to form and heterogeneous
reaction on PSCs convert chlorine reservoirs into reactive chemical species. HCl and ClONO₂ decrease occurred at both 18
25 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
distance between Syowa Station and the inner edge of the polar vortex. ~~Temporal variation of chlorine species over Syowa~~
~~Station was affected by both heterogeneous chemistry related to PSC occurrence deep inside the polar vortex, and transport of~~
30 ~~an NO_x-rich airmass from lower latitudinal polar vortex boundary region which can produce additional ClONO₂ by reaction~~
~~between ClO and NO₂.~~ 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 edge region in more detail. Rapid conversion of chlorine reservoir
species (HCl and ClONO₂) into Cl₂, gradual conversion of Cl₂ into Cl₂O₂, increase of ClO when sunlight became available,

and conversion of ClO into HCl, was successfully reproduced by the CCM. HCl decrease in the winter polar vortex core continued to occur due to the transport of ClONO₂ from the subpolar region (~~55–65°S~~) to higher latitudes (~~65–75°S~~), providing a flux of ClONO₂ from more sunlit latitudes into the polar vortex. Temporal variation of chlorine species over Syowa Station was affected by both heterogeneous chemistry related to PSC occurrence deep inside the polar vortex, and transport of an NO_x-rich air mass from lower latitudinal polar vortex boundary region which can produce additional ClONO₂ by reaction of ClO with NO₂. The deactivation pathways from active ~~chlorine~~ ClO into reservoir species (HCl and/or ClONO₂) were found to be highly dependent on the availability of ambient O₃ ~~and NO_x~~. At an altitude (18 km) where most ozone was depleted in Antarctica, most ClO was converted to HCl. However, at an altitude (22 km) when there were some O₃ ~~and NO_x~~ available, additional increases ~~super recovery~~ of ClONO₂ from initial value can occur, similar to the case in the Arctic.

1. Introduction

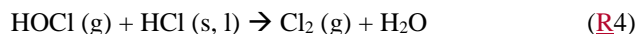
Discussion of the detection of “recovery” of the Antarctic ozone hole as the result of CFC restrictions has been attracting attention. The occurrence of the Antarctic ozone hole is considered to continue at least until the middle of this century. The world’s leading Chemistry-Climate Models (CCMs) mean time series indicate that the springtime Antarctic total column ozone will return to 1980 levels between 2045 and 2060 (WMO, 2014). In fact, the recovery time predicted by CCMs has large uncertainty, and observed ozone hole magnitude also shows ~~great~~ year-to-year variability. 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).

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+ClONO₂) and ~~inert~~ chlorines reservoirs (HCl and ClONO₂) are crucial. ~~Inert~~ eChlorine reservoir is converted to active chlorine that destroys ozone on polar stratospheric clouds (PSCs) through heterogeneous reactions:



where g, s, and l represents the gas, solid, and liquid phases, respectively (Solomon et al., 1986; Nakajima et al., 2016).

Heterogeneous reactions on the surface of particles;



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:



When the stratospheric temperatures gets warmer than nitric acid trihydrate (NAT) PSC saturation temperature, and no PSCs are present, gradual indeactivation of chlorine starts to occur. Re-formation of ClONO_2 and HCl mainly occurs through reactions:



The re-formation of ClONO_2 by reaction (R12) from active chlorine is much faster than that of HCl by reaction (R13), if there are enough NO_x around (Mellqvist et al., 2002; Dufour et al., 2006). But the formation rates of ClONO_2 and HCl are also related to ozone concentration. Douglass et al. (1995) 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:



20 High Cl/ClO ratio leads rapid HCl formation by reaction (R13) and reduces the formation ratio of ClONO_2 by reaction (R12).

The processes of indeactivation of active chlorine are different between typical conditions in the Antarctic and those in the Antarctic. In the Antarctic, the temperature cools below the PSC formation threshold in the whole area of the polar vortex in most 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 following reasons: The lack of ozone (typically less than 0.5 ppmv) by the mechanism described in the previous paragraph (Grooß et al., 2011), prevents the formation of ClO via reaction (8), and the lack of NO_2 due to denitrification prevents the formation of ClONO_2 by reaction (12).

On the other hand, in the Arctic, typically less PSC formation occurs in the polar vortex ~~occurs in the limited area of the polar vortex~~ due to generally higher stratospheric temperatures (~10-15K in average) compared with that of Antarctica. Then ~~and~~ only partial denitrification and chlorine activation occur (Manney et al., 2011; WMO, 2014). In this case, some ozone, ClO , 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 ~~in equation~~ (R12) (Michelsen et al., 1999; Santee et al., 2003), which results in additional increases ~~super-recovery~~ of ClONO_2 than initial value at the time of chlorine deactivation in spring (Webster et al., 1993). In this way, the partitioning distribution ratio of ~~inert~~ chlorine reservoir

in springtime is related to temperature, PSC amounts, ozone, and NO₂ concentrations (Santee et al., 2008; Solomon et al., 2015).

In the polar regions, the ozone and related atmospheric trace ~~gas species~~~~components~~ have been intensively monitored by several techniques since the discovery of the ozone hole. These ~~measurements~~ consist of direct observations by high-altitude aircrafts ~~observations~~ (e.g., Anderson et al., 1989; Ko et al., 1989; Bonne et al., 2000, ~~etc.~~), 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, ~~etc.~~), remote sensing observations from the ground (e.g., Farmer et al., 1987; Kreher et al., 1996; Mellqvist et al., 2002; Blumenstock et al., 2006, ~~etc.~~). 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~~~~components~~ at the same time or in a short time interval. 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 Aura/MLS and 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 course of the ozone hole formation and dissipation period. 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 are described in Section 4. Finally, in Section 5, simulated distributions of minor species simulated with ~~the~~ MIROC3.2 chemistry-climate model are used to further discuss the behavior of active and inert chlorine species.

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 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 second high-resolution FTIR site in Antarctica in operation after New Zealand's Arrival Heights facility at Scott Station (77.8°S, 166.7°E) (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), and fed by an external solar tracking system. Since Syowa Station is located at a relatively low latitude (69.0°S) compared with Scott Station (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 we can resume FTIR measurements from early spring (late July), we can measure chemical species during ozone hole development. Another advantage of Syowa Station is that we can measure

both inside and outside of the polar vortex, since the station is sometimes located near the edge of the polar vortex. From March to December 2007, we made 78 days of FTIR measurements in total. Another 19 days of FTIR measurements were performed from September to November 2011. Table 1 shows 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 Section 4 using ERA-Interim reanalysis data.

The [retrieval analysis](#) 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 ~~4730 or more~~ layers from the ground to 100 km, using the [FSCASATM](#) (Gallery et al., 1983) program for atmospheric ray-tracing to account for refractive bending. The retrieval parameters for each gas are shown in Table 2. 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 O₃, HCl, and HNO₃ 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 O₃, monthly averaged profiles from ILAS-II for HNO₃ and monthly averaged profiles from HALOE (Anderson et al., 2000) for HCl. Typical averaging kernels of the SFIT2 retrievals for O₃, HNO₃, and HCl are shown in Figures 1(a), ~~(b), and, 1(b), and 1(c)~~, respectively.

2.2 Satellite measurements

[The Earth Observing System \(EOS\) Microwave Limb Sounder \(MLS\) 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 3.3 data (Liversey et al., 2006; Santee et al., 2011; Ziemke et al., 2011; Liversey et al., 2013). [The MLS data was selected](#) whose measurement location is within 300 km radius from Syowa Station and within ±6 hours of the FTIR measurement.

[–Michelson Interferometer for Passive Atmospheric Sounding \(MIPAS\) 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 \(Fischer and Oelhaf, 1996\). 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, ..., 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 European Environmental Satellite (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~~^{whose} measurement criteria of the MIPAS data used in this study are the same as that of Aura/MLS.

~~The Cloud-Aerosol-Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) satellite was launched on 28 April 2006. On CALIPSO satellite, Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) instrument was on board, to monitor aerosols, clouds, and polar stratospheric clouds (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). In order to monitor the appearance of polar stratospheric clouds (PSCs) over Syowa Station, we used CALIOPSO PSC data (Pitts et al., 2007; 2009; 2011).~~

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 Aura/MLS version 3.3 data (Liversey et al., 2013) for 2007 measurements. 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. The ozonesonde and Aura/MLS profiles were interpolated onto a 1 km-grid, then smoothed with a 5 km-wide slit function.

Figures 2(a) ~~and 2(b)~~ show absolute and percentage differences of O₃ profiles retrieved from FTIR measurements and those from ozonesonde measurements, respectively, calculated from 14 coincident measurements from September 5 to December 17, 2007. We define the percentage difference D as:

$$D (\%) = 100 * (FTIR-sonde) / ((FTIR+sonde)/2). \quad (14)$$

The absolute agreement between 15 and 25 km was within -0.02 to 0.40 ppmv. The relative difference ~~D-value~~ between 15 and 25 km was within -10.4 to +24.4%. The mean D ~~value~~ 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 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.

Figures ~~23(ca)-and-3(db)~~ show absolute and percentage differences of HNO_3 profiles retrieved by FTIR measurements and those from Aura/MLS measurements, respectively, calculated from 44 coincident measurements. The agreement between 15 and 25 km was within -0.56 to +0.57 ppbv. The D ~~value~~-between 15 and 25 km was within -25.5 to +21.9%. The mean D ~~value~~ for HNO_3 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%. However, 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 at pressure level of 100-3.2 hPa) compared with other measurements.

Figures ~~24(ca)-and-4(fb)~~ show absolute and percentage differences of HCl profiles retrieved by FTIR measurements and those from Aura/MLS measurements, respectively, calculated from 47 coincident measurements. The agreement between 15 and 25 km was within -0.20 to -0.09 ppbv. The D ~~value~~-between 15 and 25 km was within -34.1 to -3.0%. The mean D ~~value~~ for HCl for the altitude of interest in this study (18-22 km) is -9.7%, with ~~a~~the minimum of -14.6% and ~~a~~the maximum of -3.0%. However, this negative bias of FTIR data is still within the error bars of FTIR measurements. Moreover, Livesey et al. (2013) showed Aura/MLS version 3.3 values are systematically greater than HALOE values by 10-15% with a precision of 0.2-0.6% in the stratosphere, which may partly explain the negative bias of FTIR data compared with MLS data.

Table 3 summarizes validation results of FTIR profiles compared with ozonesonde or Aura/MLS measurements, and possible Aura/MLS biases from literature.

4. Results

Figures ~~35(a)-(d)-and-5(b)~~ show ~~the time series~~temporal variations of temperatures at 18 and 22 km over Syowa Station using ERA-Interim data (Dee et al., 2011) for 2007 and 2011, ~~respectively~~. Approximate saturation temperatures for ~~nitric acid trihydrate (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 ~~were~~ identified by ~~the nearest CALIOP SO data, and data of that day were~~ indicated by asterisks on the bottom of the figures. Over Syowa Station, PSCs were observed at 15-25 km from the beginning of July (day 183) to the middle of September (day 253) in 2007, and from late June (day 175) to early September (day 251) in 2011.

PSCs were observed only below 20 km after mid-August, due to the sedimentation of PSCs and downwelling of vortex air in late winter. Although temperatures above Syowa Station ~~we~~are sometimes below T_{NAT} in June and in late September, no PSC was observed during those periods. This ~~may be~~is 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 ~~4-76, 7, 8, and 9~~ show ~~time series~~temporal variations 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. O₃ (sonde) is observed with the KC96 ozonesonde for 2007 and the ECC-1Z ozonesonde for 2011 by JMA. HCl (~~MLS~~) and HNO₃ (~~MLS~~) observed by Aura/MLS are plotted to complement the data lack of FTIR measurements. ClONO₂ is observed by Envisat/MIPAS. 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). Inferred total inorganic chlorine Cl_y* is calculated from N₂O value (in ppbv) measured by MLS using the polynomial equation derived from the correlation of Cl_y and N₂O (Bonne et al., 2000): ~~of:~~

$$\text{Cl}_y^*(\text{pptv}) = 4.7070 \cdot 10^{-7} (\text{N}_2\text{O})^4 - 3.2708 \cdot 10^{-4} (\text{N}_2\text{O})^3 + 4.0818 \cdot 10^{-2} (\text{N}_2\text{O})^2 - 4.6856 (\text{N}_2\text{O}) + 3225. \quad (245)$$

Dark shaded and thin shaded days indicate that Syowa station was located outside and in the boundary region of the polar vortex, respectively. 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 categorized into three categories; 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).

Hereafter, we will discuss the results only when Syowa station was located inside the polar vortex. Note that the Syowa station is often located near the vortex edge and the temporal variations observed over Syowa station sometimes reflect spatial variations, not the chemical evolution. 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 46(a) and 68(a)) is due to large error in Aura/MLS or Envisat/MIPAS measurements during this period.

~~Characteristics of variations in each minor species for 2007 and 2011 at altitudes of 18 and 22 km are summarized in Tables 4 (ClO), 5 (HCl), 6 (ClONO₂), 7 (Cl_y*), 8 (O₃), and 9 (HNO₃). In these tables, typical values (mixing ratios), approximate starting and ending days of decrease, variation amounts, etc. are summarized for each species. The altitude of 18 km was selected because it was the altitude where the most ozone depletion was occurred. The altitude of 22 km was selected to show the difference of the behavior of minor atmospheric species with 18 km where about half of the ozone was depleted.~~

The common features found in both 2007 and 2011 at both altitudes of 18 and 22 km can be summarized as follows: ClO ~~was~~ enhanced in August and September and the day-to-day variations were large over this period. HCl was almost zero from late June to early September and the day-to-day variations were small over this period (larger values are related to the polar vortex boundary). HCl and ClONO₂ decreased first, then ClO started to increase in winter, while HCl increases and ClO decreases were synchronized in spring. 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. O₃ decreased from July to late September when ClO was present. 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.

The following characteristics are evident especially at 18 km (Figures 46 and 57). The day-to-day variations of HCl from late June to early September were as small as 0-0.3 ppb_v. The recovered values of HCl in spring were larger than those before winter and those outside the polar vortex during the same period. ClONO₂ kept near zero even after ClO disappeared, and did not recover to the level before winter until spring. O₃ gradually decreased from values of 2.5-3 ppm_v before winter to values less than one fifth, 0.3-0.5 ppm_v, in October.

The following characteristics are evident only at 22 km (Figures 68 and 79). The day-to-day variation of HCl from late June to early September were 0-1 ppb_v, larger than those at 18 km. The recovered values of HCl in spring were nearly the same as those before winter (around 2.2 ppb_v). ClONO₂ recovered to larger values than those before winter after ClO disappeared. From winter to spring, O₃ gradually decreased, but the magnitude of the decrease was much smaller than that at 18 km.

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

Figure 79 shows that temporal ClO enhancement and decrease of O₃, ClONO₂, and HNO₃ occurred in early winter (day 150-170) at 22 km in 2011. This small ozone depletion event before winter might 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.](#)

5. Discussion

The ratios of observed HCl, ClONO₂, ClO, and Cl_y [with respect](#) to Cl_y^{*} were calculated to discuss the temporal variations of the chlorine partitioning. Here, observed Cl_y is determined as:

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

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

Figures 840 and 944 show [the time series temporal variations](#) 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. For both in 2007 and 2011 at 18 km (Figure 840), the ratio of HCl was 0.6-0.8 and the ratio of ClONO₂ was 0.2-0.3 before winter (day 130-140). The partitioning of HCl was three times larger than that of ClONO₂ at that time. The ratio of ClO increased to 0.5-0.6 during the enhanced period (day 240-260). The ratio of HCl was 0-0.2 and the ratio of ClONO₂ was 0-0.6 during this same period. ClONO₂ shows negative correlation with ClO, while HCl kept low even when ClO was low during this period. This negative correlation is shown in Figure 102 later. When ClO was enhanced, the O₃ amount gradually decreased, and finally reached <0.5 ppmv (>80% destruction) in October (day

280) (See Figures 46 and 57). The ratios became 0.9-1.0 for HCl and 0-0.1 for ClONO₂ after the recovery in spring (after day 290), indicating that almost all chlorine reservoir species became HCl via reaction (R13), due to the lack of O₃ and NO₂ during this period. The ratios of Cl_y (FTIR) and Cl_y (MLS) were both around 0.7 at the time of ClO enhanced period (day 230-260). The remaining chlorine are thought to be Cl₂O₂, which will be shown in model simulation in Section 5 later. The ratio of Cl_y values became close to 1 after the recovery period (after day 280).

For both in 2007 and 2011 at 22 km (Figure 944), the ratio of HCl was 0.4-0.9 and the ratio of ClONO₂ was 0.2-0.3 before winter (day 110-140). The partitioning of HCl was two to three times larger than that of ClONO₂. The ratio of ClO increased to 0.6-0.7 during the enhanced period (day 220-240). The ratio of HCl was 0-0.3 and the ratio of ClONO₂ was 0-0.6 during this period. ClONO₂ shows negative correlation with ClO, while HCl kept low even when ClO was low during this period like the case at 18 km. The O₃ amount gradually decreased during the ClO enhanced ~~period, but~~ remained >1.5 ppmv (less than half destruction) at this altitude (See Figures 68 and 79). When the ClO enhancement ended, temporal increase (~~super recovery~~) of ClONO₂ up to a ratio of 0.5 occurred in early spring (day 260-280). Then, the reservoir ratios became 0.6-0.8 for HCl and 0.2-0.4 for ClONO₂ in spring (after day 280). This phenomenon shows that more chlorine deactivation via reaction (R12) occurred towards ClONO₂ at 22 km rather than at 18km. This is attributed to the existence of O₃ and NO₂ during this period at 22 km, which was different from the case at 18 km. The ratios of Cl_y (FTIR) and Cl_y (MLS) were both around 0.8 at the time of ClO enhanced period (day 230-250). The remaining chlorine are thought to be Cl₂O₂. The ratio of Cl_y values became around 1.1 after the recovery period (after day 270). The reason why observed Cl_y values exceed calculated Cl_y* values might be due to the difference in N₂O-Cl_y correlation at this altitude from the one in which are used to calculate Cl_y* value by using the equation (2).

In 2011 at 18 km (Figure 840), another temporal increase of ClONO₂ up to a ratio of 0.6 occurred in early spring (around day 280) in accordance with HCl increase, then the ClONO₂ amount gradually decreased to nearly zero after late October (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 always located inside the polar vortex from day 195 to 350, the difference between the equivalent latitude over Syowa Station and that at inner edge became less than 10 degrees at around day 280, while it was typically between 15 and 20 degrees in other days. O₃ and HNO₃ showed higher values around day 280 (see Figure 57), indicating that Syowa Station was located close to the boundary region at this period. Therefore, the temporal increase of ClONO₂ in 2011 at 18 km was attributed to spatial variation, not to chemical evolution.

5. Discussion

Figure 102 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). Note that MLS ClO and MIPAS ClONO₂

data were sampled on the same day at the nearest orbit for both satellites to Syowa Station. 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) regression. Negative correlations of slope ~ -1.0 between CIO and ClONO₂ are seen in all figures. The cause of this negative correlation might be due to the variation of the relative distance between Syowa Station and the boundary region of the polar vortex. When Syowa Station was located deep inside the polar vortex, there was more CIO and less ClONO₂. On the contrary when Syowa Station was located near the vortex edge, there was less CIO and more ClONO₂. The potential vorticities (PV) over Syowa Station shown by color code generally show this tendency, that warm colored higher PV points are located more towards bottom right-hand side. This is further confirmed by 3D model simulation as is shown later in this section.

Figures 13, 14, 15, and 16 show simulated mixing ratios of O₃ (a), NO₂ (b), HNO₃ (c), CIO (d), HCl (e), and ClONO₂ (f) by the MIROC3.2 Chemistry-Climate Model (CCM) at 50 hPa (~18 km) for June 24 (day 175), September 1 (day 244), September 6 (day 249), and October 6 (day 279) in 2007, respectively. For a description of the MIROC3.2 CCM, please see Appendix A for detail. The location of Syowa Station is shown by a white star in each panel. Direct comparisons of mixing ratios of CIO, HCl, ClONO₂, Cl_y, and O₃ measured by FTIR and MLS, and modeled by MIROC3.2 CCM in 2007 and 2011 at 18 and 22 km are shown in Appendix B. In general, the model results are in good agreement with FTIR and satellite observations (Figure B1). Hereafter, the result of MIROC3.2 CCM is discussed.

On June 24 (day 175, Figure 13), stratospheric temperatures over Antarctica were already low enough to allow PSCs to form. Consequently, NO₂ and HNO₃ in the polar vortex condensed onto PSCs (Figures 13(b) and 13(c)). Note that the depleted area of NO₂ was greater than that of HNO₃. This might be due to reaction (R12) that converts CIO and NO₂ to ClONO₂ at the edge of the polar vortex, which is shown by the enhanced ClONO₂ area at the vortex edge in Figure 13(f). 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 (Figures 13(e) and 13(f)). Some HCl remains near the core of the polar vortex (Figure 13(e)), because the initial amount of the counter-part of heterogeneous reaction (R1) (ClONO₂) was less than that of HCl (see Figure 46 and/or 57). The O₃ amount was only slightly depleted within the polar vortex on this day (Figure 13(a)).

On September 1 (day 244, Figure 14), amounts of NO₂ (Figure 14(b)), HNO₃ (Figure 14(c)), HCl (Figure 14(e)), and ClONO₂ (Figure 14(f)) all show very depleted values in the polar vortex. The amount of CIO (Figure 14(d)) shows some enhanced values at the outer part of the polar vortex. About 50% Development of ozone depletion was seen throughout in the polar vortex. Note that ClONO₂ (Figure 14(f)) 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 244), Syowa Station was located inside the polar vortex close to the inner vortex edge, where CIO was smaller and ClONO₂ was greater than the values deep inside the polar vortex.

On September 6 (day 249, Figure 15), most features were the same as on September 1, but the shape of the polar vortex was different. Consequently, Syowa Station was located deep inside the polar vortex, where CIO was greater and ClONO₂ was smaller than the values around the boundary region of the polar vortex. Hence, the negative correlation between CIO and

ClONO₂ seen in Figure 102 was due to variation of the relative distance between Syowa Station and the inner edge of the polar vortex.

On October 6 (day 279, Figure 16), ClO enhancement has almost disappeared (Figure 16(d)). Inside the polar vortex, depletion of O₃ (Figure 16(a)), NO₂ (Figure 16(b)), HNO₃ (Figure 16(e)), and ClONO₂ (Figure 16(f)) showed very low values continued. Ozone was almost fully destroyed at this altitude in the polar vortex. However, the amount of HCl (Figure 16(e)) increased deep inside the polar vortex. This might be due to the recovery of HCl by reaction (R13) deep inside the polar vortex, where there is no O₃ or NO₂ left and reaction (R13) was favored compared with reaction (R12). At Syowa Station, the amount of HCl was several times greater than that of ClONO₂ on this day.

Three-hourly time series temporal evolution of zonal-mean active chlorine species, Cl₂O₂ (b), Cl₂ (c), ClO (d), and their sum (ClO+2*Cl₂O₂+2*Cl₂) (a), and chlorine reservoir species HCl (e) and ClONO₂ (f) modeled by MIROC3.2 CCM at 68.4°S, 71.2°S, 76.7°S, and 87.9°S are plotted in Figure 127. The dates on which the distribution of each species is shown in Figures 113-16, are indicated by vertical dotted lines. In this figure, it is shown that HCl and ClONO₂ rapidly decreased at around day 130 at 87.9°S, when PSCs started to form in the Antarctic polar vortex (Figures 127(e) and 127(f)). The decrease of HCl stopped when the counter-part of the heterogeneous reaction (R1) was missing at around day 140. Consequently, Cl₂ was formed (Figures 127(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 day 150-160 (Figures 127(b) and 127(c)), through reactions (R5), (R8), and (R9). At the higher latitude (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 after winter (day 190 or later), because sun light is needed to form ClO by reactions (R5) and (R8) in the polar vortex (Figure 127(d)). Nevertheless, there were some enhancements of ClO in early winter, day 175, simulated at the edge of the polar vortex (Figure 113(d)) 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 day 195, towards higher latitude (87.9°S) at around day 255 (Figure 127(d)). Diurnal variation of ClO was also seen at latitudes between 68.4°S and 76.7°S. When stratospheric temperature increased above PSC saturation temperature at around day 270 (Figure 35(a)), chlorine activation ended, and ClO was mainly converted into HCl at all latitudes inside the polar vortex (Figures 127(d) and 127(e)). This is because reaction (R13) occurs more frequently than reaction (R12) inside the polar vortex, as there was little NO₂ available due to the depleted O₃ amount there as was described in Section 1 (Douglass et al., 1995).

Continuous loss of HCl was seen at 87.9°S between days 160 and 200 even after the disappearance of the counterpart of heterogeneous reaction (R1) (Figure 127(e)). 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 the formation of NO_x due to galactic cosmic rays during the winter polar vortex (Grooß et al., 2018). Solomon et al. (2015) proposed a new mechanism on this issue: Continuous transport of ClONO₂ from the 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. Our result also shows the same phenomena indicated by some sporadic increase in ClONO₂ at around days 158, 179, and 189 at 76.7°S as shown in Figure

127(f). Subsequently, HCl losses were observed at 76.7°S and 87.9°S during these episodes in Figure 127(e). The continuous loss of HCl at the most polar latitude (87.9°S) might be due to the gradual mixing of air within the polar vortex during the winter period, when polar vortex was still strong.

5 6. Summary/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 related to the ozone hole from the ground in Antarctica. Retrieved profiles were validated with Aura/MLS and ozonesonde data. The absolute differences between FTIR and Aura/MLS or
10 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 below PSC saturation temperature, PSCs started to form and heterogeneous reaction between HCl and ClONO₂ occurred and ClONO₂ was
15 almost completely lost 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 distance between Syowa Station and the inner edge of the polar vortex. ~~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 airmass from lower latitudinal polar vortex boundary region, which can produce additional ClONO₂ by reaction (12).~~
20

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. ~~In general, the modeled O₃ and day-to-day variations of HCl and ClONO₂ results~~ are 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 ClO when sunlight became available, and
25 conversion of ClO into HCl were successfully reproduced by the CCM. HCl decrease in the winter polar vortex core continued to occur due to the transport of ClONO₂ from the subpolar region (~~55–65°S~~) to higher latitudes (~~65–75°S~~), providing a flux of ClONO₂ from more sunlit latitudes into the polar vortex. ~~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 airmass from lower latitudinal polar vortex boundary region, which can produce additional ClONO₂ by reaction (R12).~~

30 The deactivation pathways from active ClO into reservoir species (HCl and/or ClONO₂) were found to be very dependent on the availability of ambient O₃ ~~and NO_x~~. 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 were some O₃ ~~and NO_x~~ available, additional increases super-

recovery of ClONO₂ than initial value can occur, like it is the case in the Arctic, through reactions (R14) and (R12) (Douglass et al., 1995).

Appendix A. MIROC3.2 nudged chemistry–climate model

5 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
10 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. The chemical constituents included in this model are O_x, HO_x, NO_x, ClO_x, BrO_x, hydrocarbons for methane oxidation, heterogeneous
15 reactions for sulfuric-acid aerosols, supercooled ternary solutions, nitric-acid trihydrate, and ice particles. The CCM contains 13 heterogeneous reactions on multiple aerosol types as well as gas-phase chemical reactions and photolysis reactions. The reaction-rate and absorption coefficients are based on JPL–2010 (Sander et al., 2010). See Akiyoshi et al. (2016) for more details.

20 Appendix B. Direct comparisons of mixing ratios of ClO, HCl, ClONO₂, Cl_y, and O₃ measured by FTIR and MLS, and modeled by MIROC3.2 CCM

Mixing ratios of several minor species measured by FTIR, Aura/MLS, and Envisat/MIPAS, are compared with values modeled by MIROC3.2 CCM. Figure B1 shows daily time series of measured and modeled ClO, HCl, ClONO₂, Cl_y, and O₃ over Syowa Station at 18 km in 2007 (Figures B1(a)–(e)), and in 2011 (Figures B1(f)–(j)). Figure B2 shows similar values at 22 km. In
25 these figures, Cl_y by Aura/MLS represents the Cl_y* value defined by equation (245) using the N₂O value measured by Aura/MLS. Cl_y from the MIROC3.2 CCM is the sum of total reactive chlorines, i.e., $\text{Cl}_y = \text{Cl} + 2*\text{Cl}_2 + \text{ClO} + 2*\text{Cl}_2\text{O}_2 + \text{OCIO} + \text{HCl} + \text{HOCl} + \text{ClONO}_2 + \text{ClNO}_2 + \text{BrCl}$.

Note that measured ClO values by Aura/MLS show daytime values, while modeled ones by the MIROC3.2 CCM are daily average, which are usually smaller than daytime values, because most ClO is converted to Cl₂O₂ by reaction (R9) during
30 nighttime. Also, modeled HCl and Cl_y showed systematically smaller values compared with FTIR or MLS measurements. The cause of this discrepancy may be 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). Nevertheless, day-to-day relative variations of measured HCl and ClONO₂ are fairly well reproduced 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.

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Tables

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 2. Retrieval parameters of SFIT2

Species	O ₃	HNO ₃	HCl
Spectroscopy	HITRAN 2008	HITRAN 2008	HITRAN 2008
PT 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

Table 3. Summary of validation results of FTIR profiles compared with ozonesonde and Aura/MLS measurements, and possible Aura/MLS biases from literatures

	D-value (%) 18-22 km	Min/Max (%) 18-22 km	Agreement 15-25 km (ppm_v/ppb_v)	Literature values
O₃	+6.2	-10.4/+19.2	-0.02~+0.40	
HNO₃	+13.2	+0.2/+21.9	-0.56~+0.57	Aura/MLS no bias with errors (0.6 ppb _v) (Livesey et al., 2011)
HCl	-9.7	-14.6/-3.0	-0.2~+0.09	Aura/MLS > HALOE by 10-15%, precision 0.2-0.6 ppb _v (Livesey et al., 2013)

Table 4. Summary of minor atmospheric species ~~CIO~~ variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
<u>Period when CIO = 0 (day)</u>	<u>-190</u>	<u>-200</u>	<u>-140</u>	<u>-150</u>
<u>Period of enhanced CIO (day)</u>	<u>230-260</u>	<u>230-260</u>	<u>220-240</u>	<u>230-250</u>
<u>Variation when CIO enhanced (ppbv)</u>	<u>0-1.3</u>	<u>0-1.5</u>	<u>0-2.2</u>	<u>0-2.2</u>
<u>HCl value before winter (ppbv)</u>	<u>1.5-1.8</u>	<u>1.2-1.6</u>	<u>2.1-2.4</u>	<u>1.8-2.2</u>
<u>HCl starting-ending day of decrease (day)</u>	<u>140-180</u>	<u>140-180</u>	<u>130-180</u>	<u>140-170</u>
<u>Variation when HCl ~ 0 (ppbv)</u>	<u>0-0.3</u>	<u>0-0.3</u>	<u>0.1-1.0</u>	<u>0.1-0.9</u>
<u>HCl starting-ending day of increase (day)</u>	<u>250-300</u>	<u>250-300</u>	<u>240-280</u>	<u>240-300</u>
<u>HCl Value after increase (ppbv)</u>	<u>2.6-3.0</u>	<u>2.5-2.8</u>	<u>2.1-2.4</u>	<u>2.0-2.5</u>
<u>HCl Value outside polar vortex (ppbv)</u>	<u>1.5-2.0</u>	<u>1.0-1.8</u>	<u>1.5-2.0</u>	<u>1.5-2.0</u>
<u>CIONO₂ Value before winter (ppbv)</u>	<u>~0.5</u>	<u>~0.4</u>	<u>0.6-0.9</u>	<u>0.6-0.7</u>
<u>Variation when CIONO₂~0 (ppbv)</u>	<u>0-1.5</u>	<u>0-1.5</u>	<u>0-2.0</u>	<u>0-2.0</u>
<u>Day of CIONO₂ enhancement</u>	<u>±</u>	<u>270-300</u>	<u>270-280</u>	<u>270-280</u>
<u>Value of CIONO₂ enhancement (ppbv)</u>	<u>±</u>	<u>1.5</u>	<u>1.5</u>	<u>1.5</u>
<u>CIONO₂ value after enhancement (ppbv)</u>	<u>0-0.3</u>	<u>0-0.2</u>	<u>0.8-1.3</u>	<u>0.8-1.1</u>
<u>CIONO₂ value outside polar vortex (ppbv)</u>	<u>0.3-0.4</u>	<u>0.2-0.3</u>	<u>0.5-0.7</u>	<u>0.6-0.8</u>
<u>O₃ value before winter (ppmv)</u>	<u>2.5</u>	<u>2.5</u>	<u>4.0</u>	<u>4.0</u>
<u>O₃ starting-ending day of decrease (day)</u>	<u>190-280</u>	<u>200-270</u>	<u>170-260</u>	<u>170-270</u>
<u>O₃ minimum value (ppmv)</u>	<u>0.3</u>	<u>0.5</u>	<u>2.0</u>	<u>1.0</u>
<u>O₃ value after recovery (ppmv)</u>	<u>0.8</u>	<u>0.8</u>	<u>2.4-4.0</u>	<u>2.0-3.5</u>
<u>HNO₃ value before winter (ppbv)</u>	<u>6-10</u>	<u>8-10</u>	<u>15-16</u>	<u>13-15</u>
<u>HNO₃ starting-ending day of decrease (day)</u>	<u>160-190</u>	<u>150-180</u>	<u>140-180</u>	<u>150-180</u>
<u>HNO₃ minimum value (ppbv)</u>	<u>0</u>	<u>0</u>	<u>2</u>	<u>1</u>
<u>HNO₃ value after recovery (ppbv)</u>	<u>3-4</u>	<u>3-4</u>	<u>4-6</u>	<u>4-5</u>
<u>Day when CIO gets 0 (day)</u>	<u>280</u>	<u>290</u>	<u>280</u>	<u>280</u>

Table 5. Summary of HCl variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
Value before winter (ppbv)	1.5–1.8	1.2–1.6	2.1–2.4	1.8–2.2
Starting day of decrease (day)	140	140	130	140
Ending day of decrease (day)	180	180	180	170
Variation when HCl = 0 (ppbv)	0–0.3	0–0.3	0.1–1.0	0.1–0.9
Day when HCl starts to increase	250	250	240	240
Day when HCl increase stops	300	300	280	300
Value after increase (ppbv)	2.6–3.0	2.5–2.8	2.1–2.4	2.0–2.5
Value outside polar vortex (ppbv)	1.5–2.0	1.0–1.8	1.5–2.0	1.5–2.0

Table 6. Summary of ClONO₂ variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
Value before winter (ppbv)	~0.5	~0.4	0.6–0.9	0.6–0.7
Starting day of decrease (day)	160	— (after 150)	160	between 140–150
Ending day of decrease (day)	— (after 170)	-	-	160
Variation when ClONO ₂ ~0 (ppbv)	0–1.5	0–1.5	0–2.0	0–2.0
Day of ClONO ₂ enhancement	-	270–300	270–280	270–280
Value of ClONO ₂ enhancement (ppbv)	-	1.5	1.5	1.5
Value after enhancement (ppbv)	0–0.3	0–0.2	0.8–1.3	0.8–1.1
Value outside polar vortex (ppbv)	0.3–0.4	0.2–0.3	0.5–0.7	0.6–0.8

Table 7. Summary of Cl_y* variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
Value before winter (ppbv)	2.3	2.2	2.8	2.9
Value after winter (ppbv)	3.1	2.9	3.2	3.2
Value outside polar vortex (ppbv)	1.5–2.0	1.5–2.0	2.4–2.6	2.2–2.8

Table 8. Summary of O₃ variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
Value before winter (ppmv)	2.5	2.5	4.0	4.0
Starting day of decrease (day)	190	200	170	170
Ending day of decrease (day)	280	270	260	270
Minimum value (ppmv)	0.3	0.5	2.0	1.0
Value after recovery (ppmv)	0.8	0.8	2.4–4.0	2.0–3.5

Table 9. Summary of HNO₃ variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
Value before winter (ppbv)	6-10	8-10	15-16	13-15
Starting day of decrease (day)	160	150	140	150
Ending day of decrease (day)	190	180	180	180
Minimum value (ppbv)	0	0	2	1
Value after recovery (ppbv)	3-4	3-4	4-6	4-5
Variation during decrease (ppbv)	0-11 (day 200-250)	0-8 (day 210-240)	2-14 (day 180-240)	1-11 (day 200-240)
Variation during decrease (ppbv)	1-5 (day 250-300)	2-4 (day 240-300)	2-6 (day 240-320)	2-8 (day 240-300)

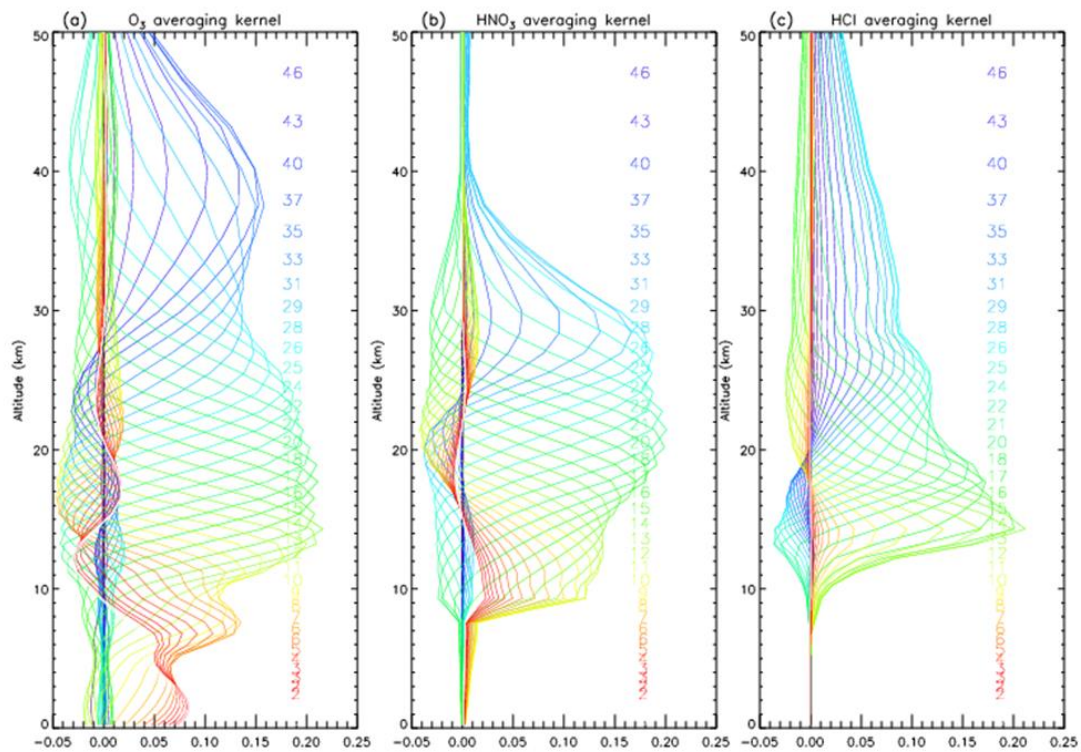


Figure 1. Averaging kernel functions of the SFIT2 retrievals for O_3 (a), HNO_3 (b), and HCl (c).

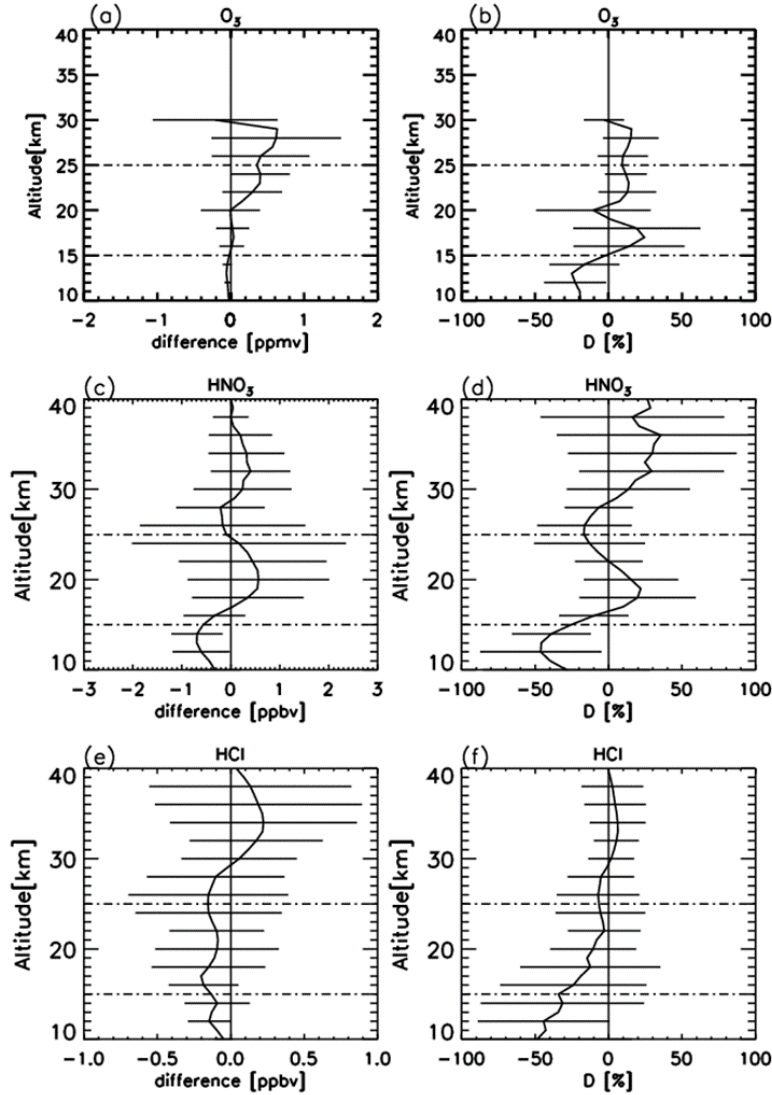


Figure 2. Absolute (a) and percentage (b) differences of O₃ profiles retrieved from FTIR measurements and those from ozonesonde measurements. Horizontal bars indicate the standard deviation of differences at each altitude. Absolute (c) and percentage (d) differences of HNO₃ profiles retrieved from FTIR measurements and those from Aura/MLS measurements. Absolute (e) and percentage (f) differences of HCl profiles retrieved from FTIR measurements and those from Aura/MLS measurements.

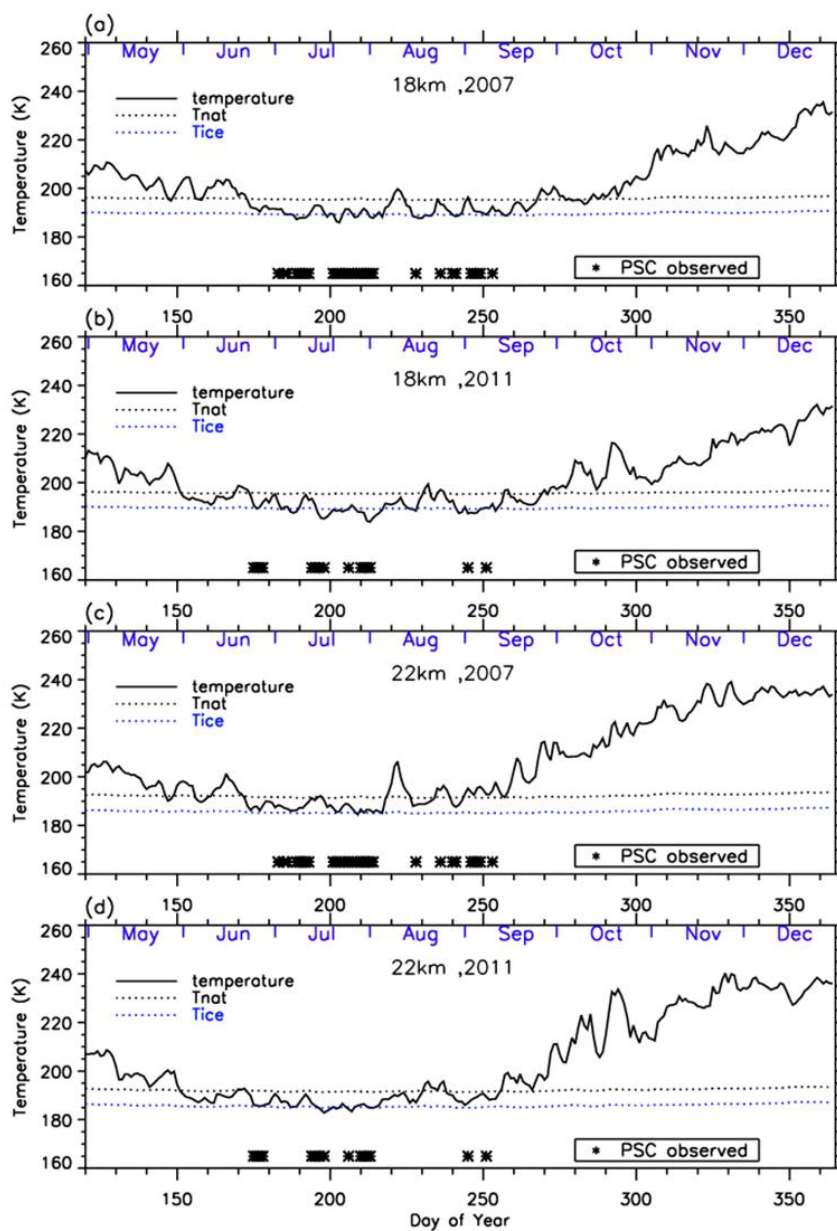


Figure 35. Time series temporal variation of temperatures at 18 km in (a) 2007 and (b) 2011, and at 22 km in (c) 2007 and (d) 2011 over Syowa Station using ERA-Interim data. Approximate saturation temperatures for nitric acid trihydrate PSC (T_{NAT}) and ice PSC (T_{ICE}) calculated by assuming 6 ppbv 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.

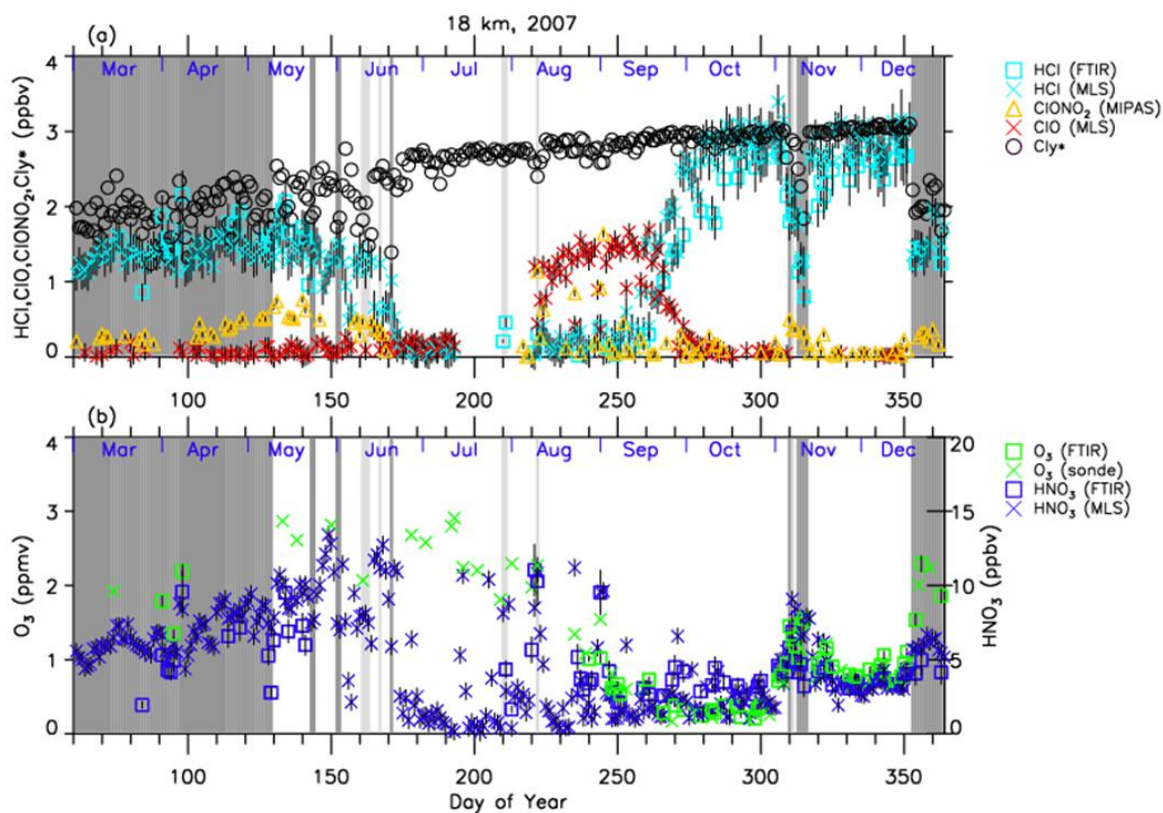


Figure 46. Time series of temporal variations of (a) HCl, ClONO₂, ClO, Cl₂*, (b) O₃, and HNO₃ mixing ratios at 18 km in 2007 over Syowa Station. O₃(FTIR), HCl(FTIR), and HNO₃(FTIR) were measured by FTIR at Syowa Station, while HCl(MLS), ClO, and HNO₃(MLS) were measured by Aura/MLS. O₃(sonde) was measured by ozonesonde. ClONO₂ was measured by Envisat/MIPAS. Cl₂* is calculated from N₂O value. See text in detail. The unit of O₃ is ppmv and the other gases are ppbv. The light and dark shaded areas are the days when Syowa Station was at the boundary region and outside the polar vortex, respectively.

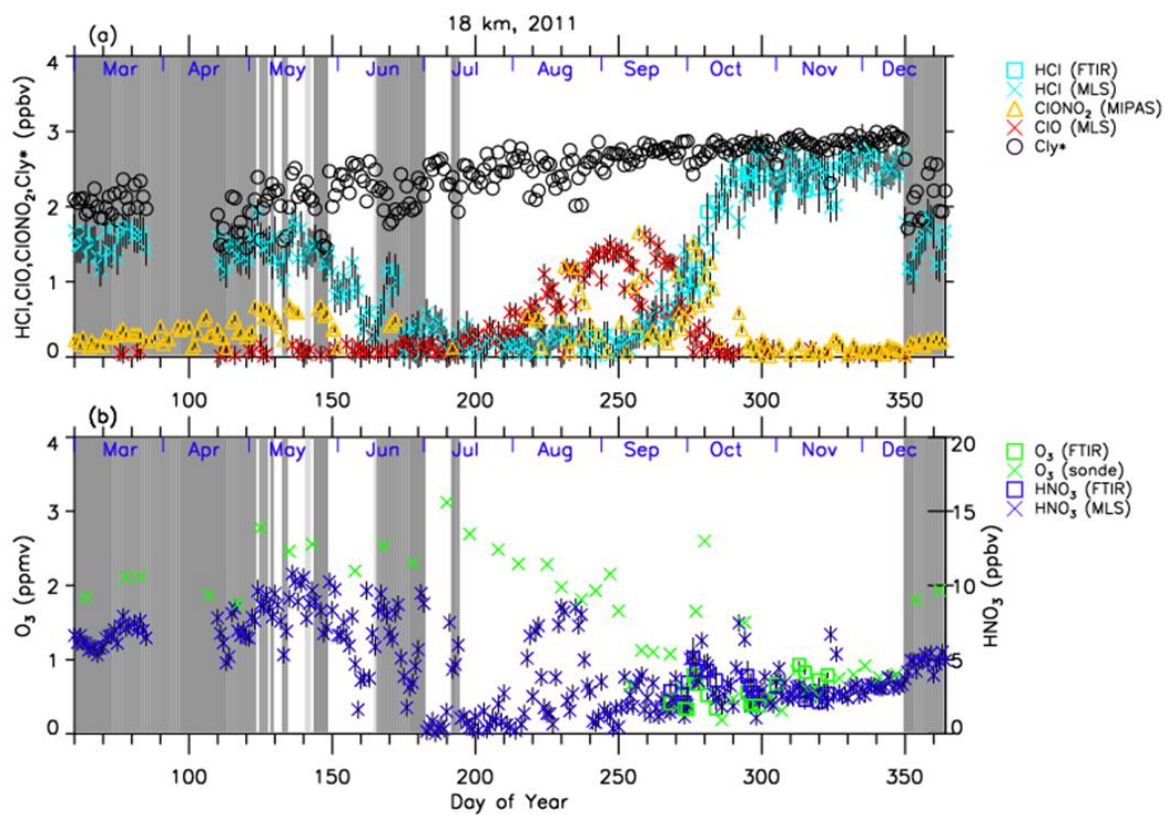


Figure 57. Same as Figure 46 but in 2011.

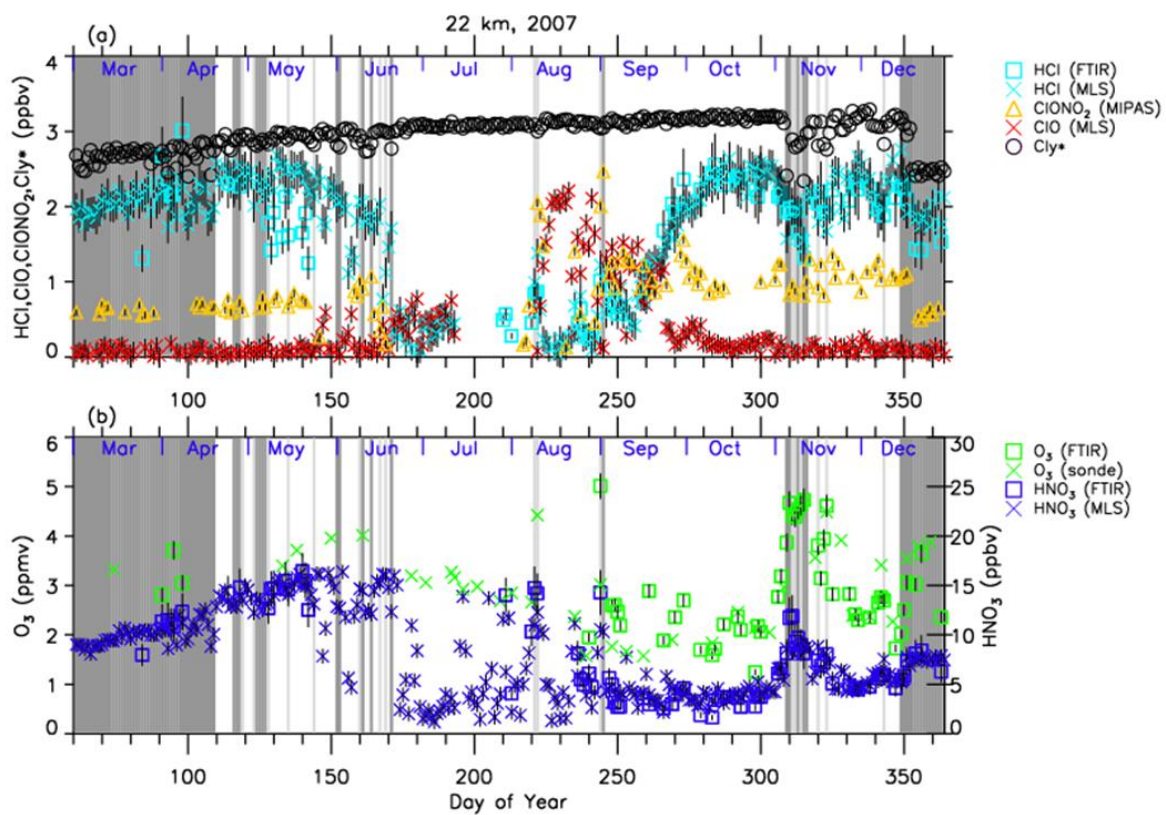


Figure 68. Same as Figure 46 but at 22 km.

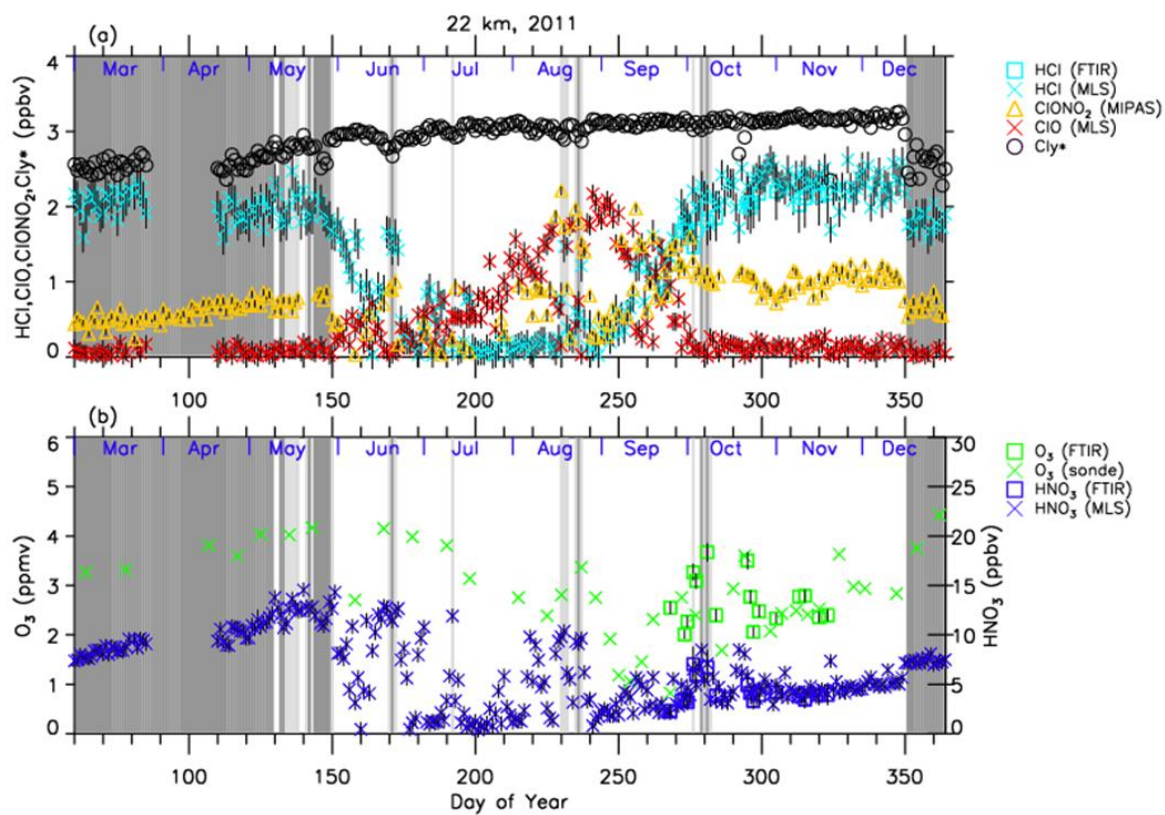


Figure 79. Same as Figure 57 but at 22 km.

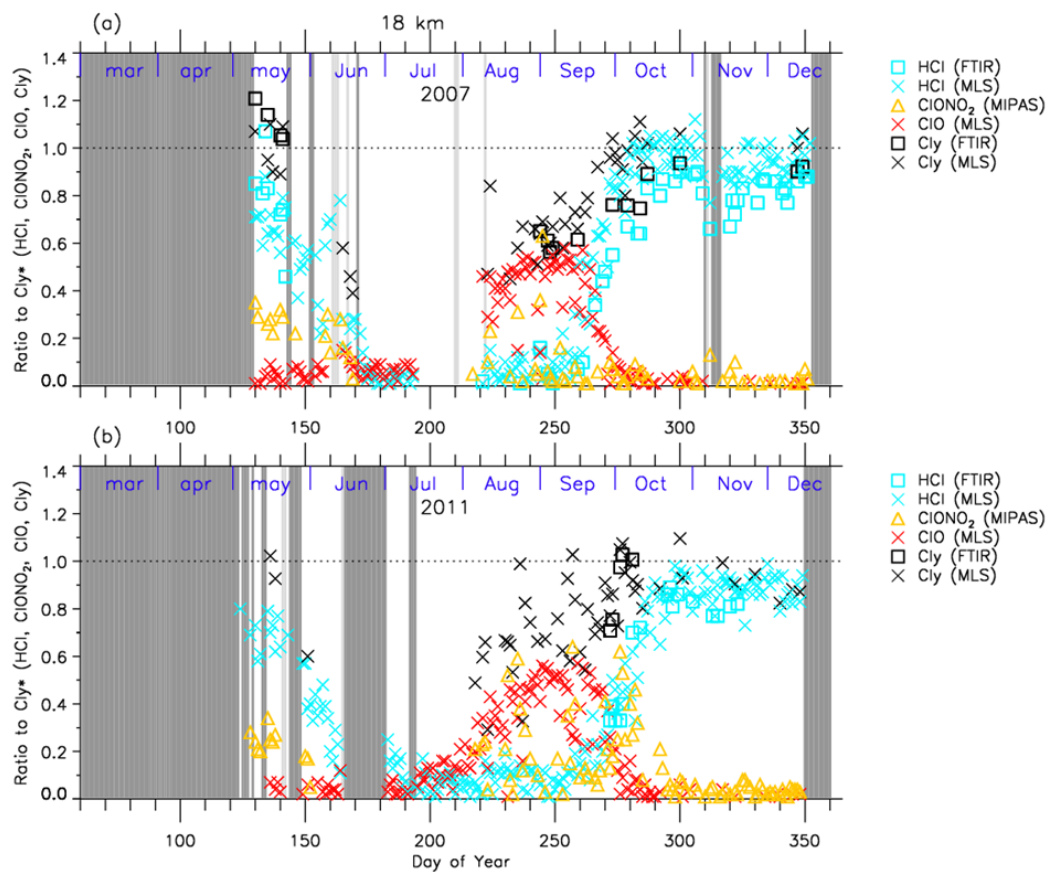


Figure 840. Time series temporal variations of the ratios of HCl, ClONO₂, ClO, and Cl_y(=HCl+ClONO₂+ClO) to total chlorine (Cl_y*) over Syowa Station at 18 km in (a) 2007 and in (b) 2011. Shaded areas are the same as Figure 46.

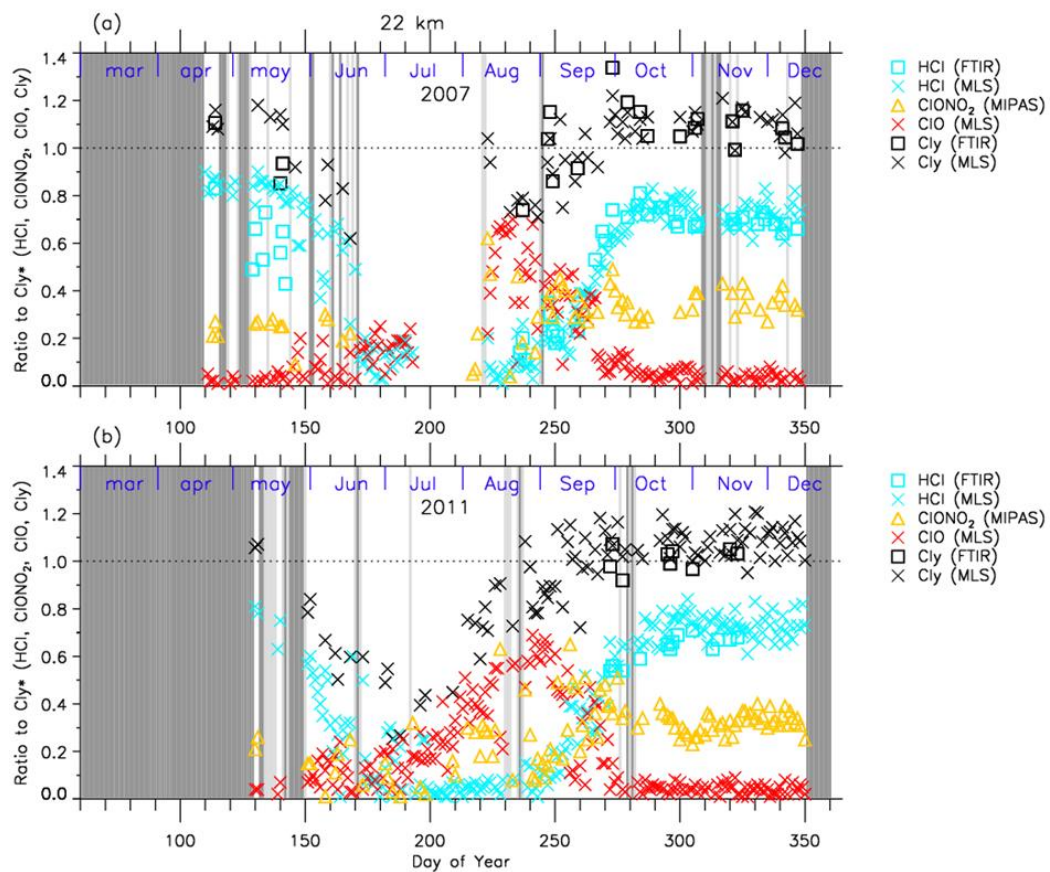


Figure 944. Same as Figure 840 but at 22 km.

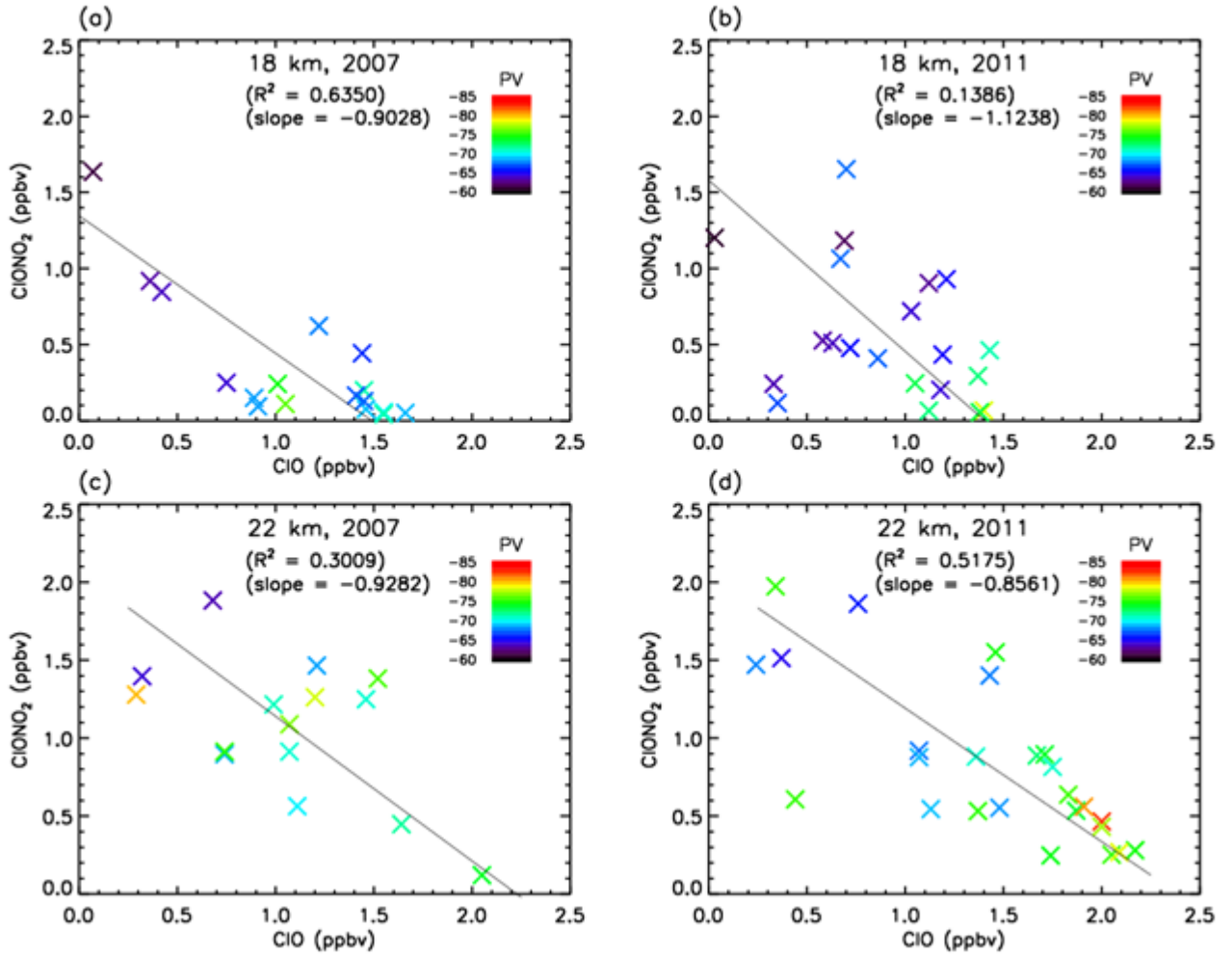


Figure 102. Scatter plot between ClO (Aura/MLS) and ClONO₂ (Envisat/MIPAS) mixing ratios between during August 8 and September 17 (day ~~number~~ 220 – 260) at 18 km and 22 km in 2007 and 2011. Solid lines are regression lines obtained by RMA (Reduced Major Axis) regression. Color represents the potential vorticity over Syowa Station on that day.

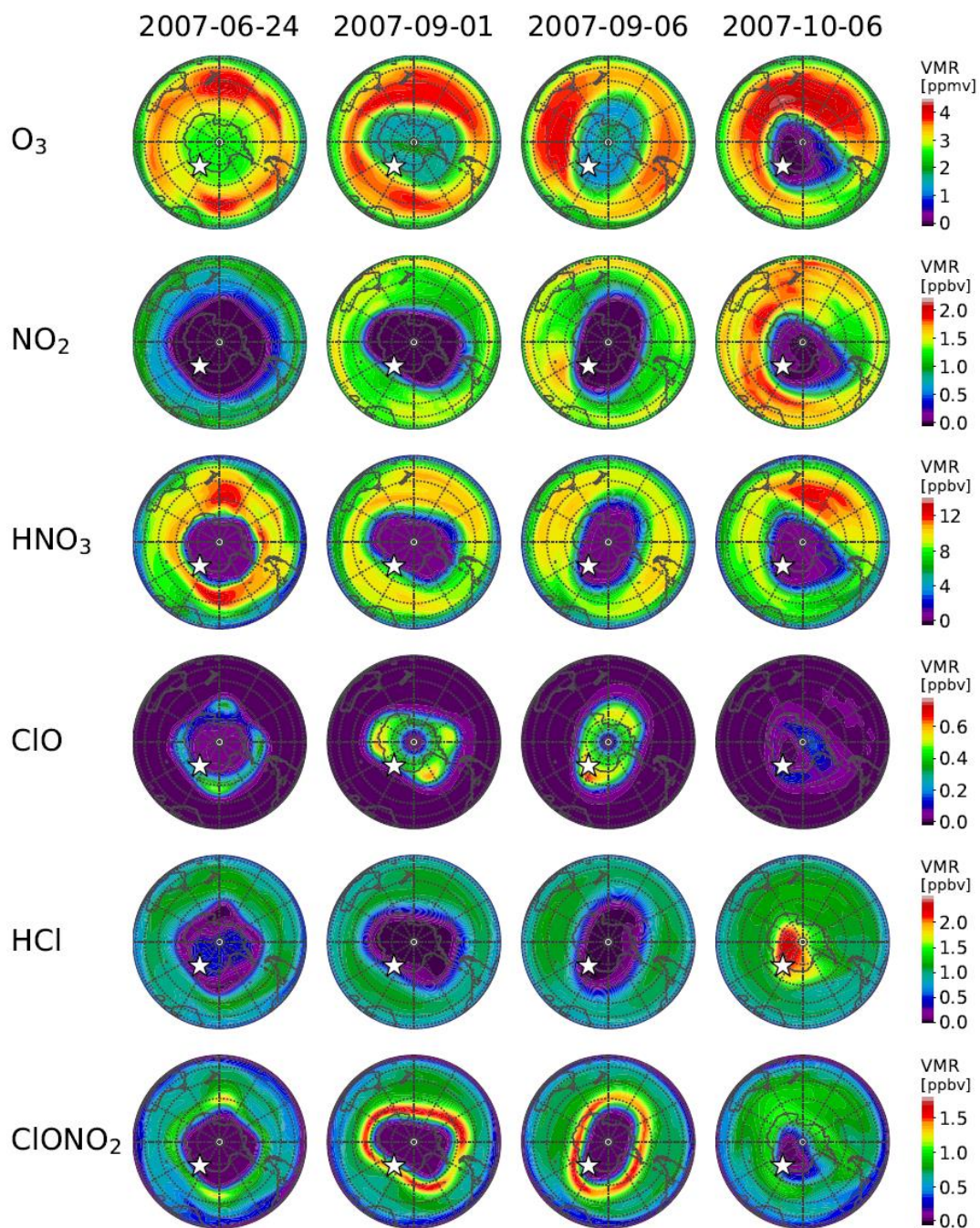


Figure 13. Polar southern hemispheric plot for simulated mixing ratios of O_3 (a), NO_2 (b), HNO_3 (c), ClO (d), HCl (e), and $ClONO_2$ (f) by a MIROC3.2 chemistry-climate model (CCM) at 50 hPa for June 24 (day 175), [September 1 \(day 244\)](#), [September 6 \(day 249\)](#), and [October 6 \(day 279\)](#), 2007. The location of Syowa Station is shown by white star in each panel.

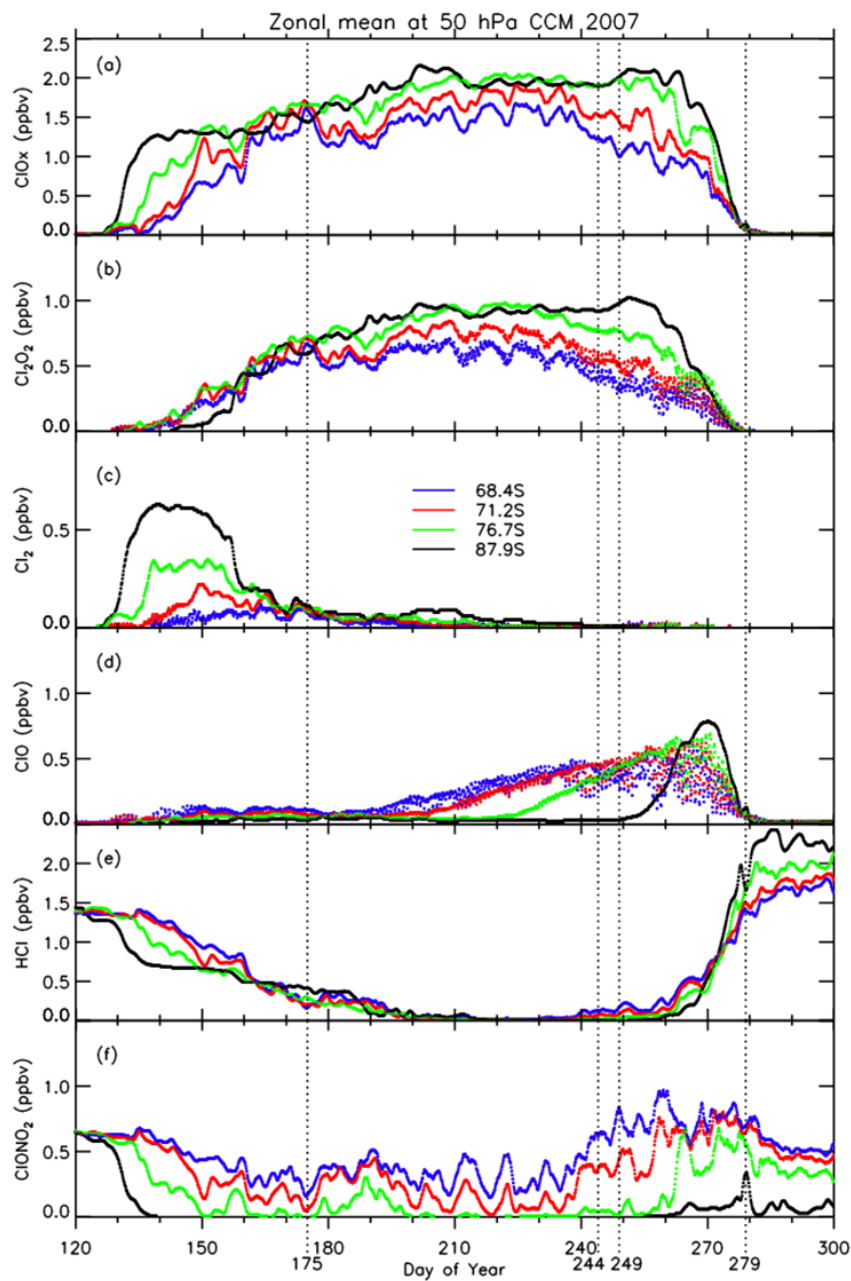


Figure 127. Three-hourly zonal-mean [time series](#) temporal variations of MIROC3.2 CCM outputs for (a) $\text{ClO} + 2 \cdot \text{Cl}_2\text{O}_2 + 2 \cdot \text{Cl}_2$, (b) Cl_2O_2 , (c) Cl_2 , (d) ClO , (e) HCl , and (f) ClONO_2 during day number 120 – 300 at 50 hPa in 2007.

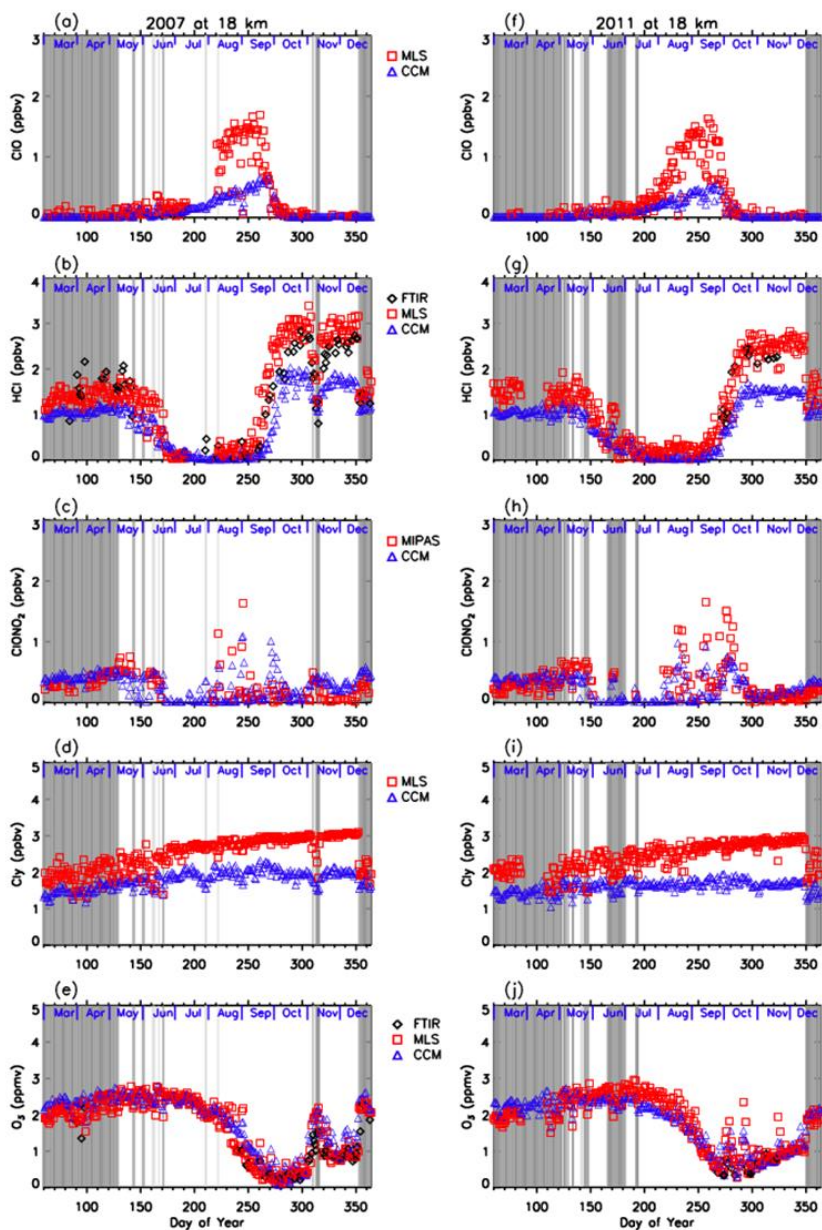


Figure B1. Daily time series of measured and modeled minor species over Syowa Station at 18 km. Black diamonds are data by FTIR, red squares are by Aura/MLS and Envisat/MIPAS, blue triangles are data by MIROC3.2 CCM. Figure B1(a) is for CIO, B1(b) is for HCl, B1(c) is for ClONO₂, B1(d) is for Cly, and B1(e) is for O₃ in 2007. Figure B1(f) is for CIO, B1(g) is for HCl, B1(h) is for ClONO₂, B1(i) is for Cly, and B1(j) is for O₃ in 2011.

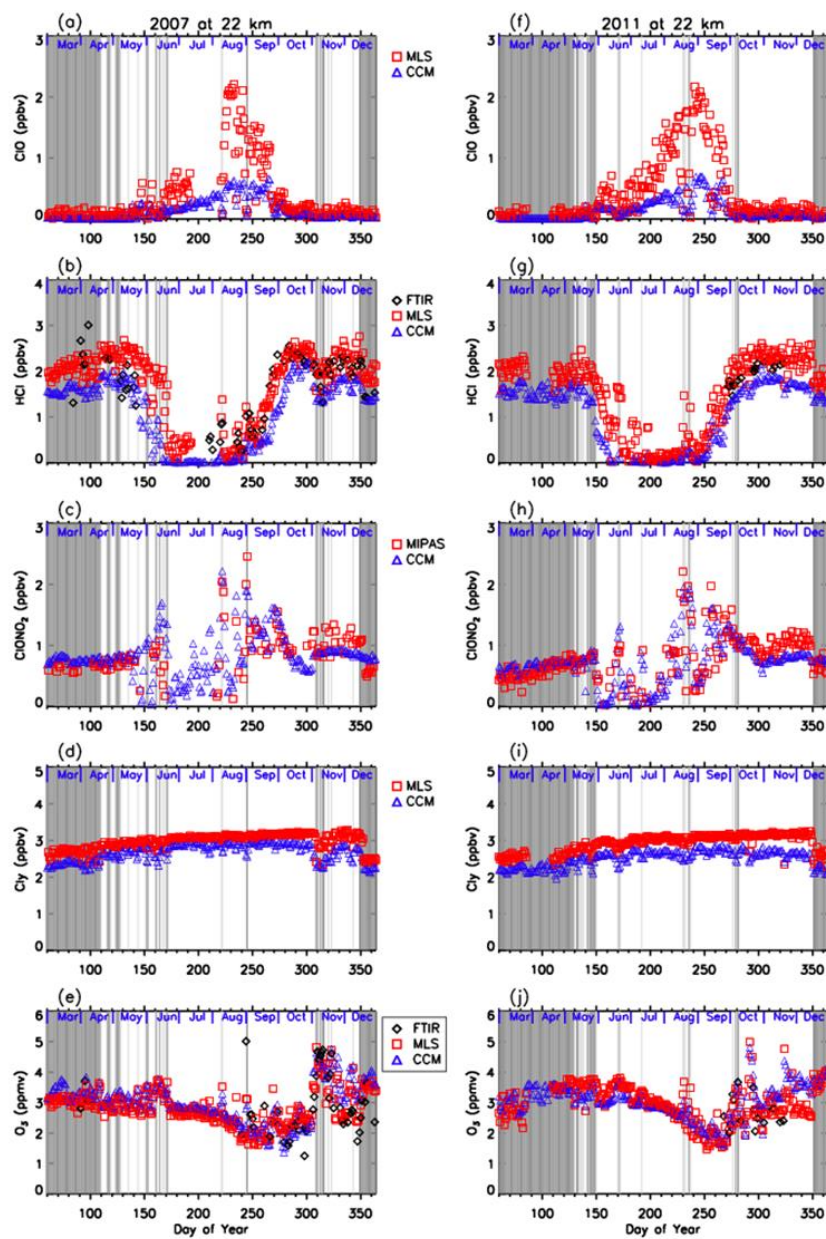


Figure B2. Same as Figure B1 but for 22 km.