# Temporal evolution of chlorine and minor species related to ozone depletion at Syowa Station, Antarctica during austral fall to spring in 2007 and 2011

Hideaki Nakajima<sup>1,2</sup>, Isao Murata<sup>2</sup>, Yoshihiro Nagahama<sup>1</sup>, Hideharu Akiyoshi<sup>1</sup>, Kosuke Saeki<sup>2,3</sup>, Masanori Takeda<sup>2</sup>, Yoshihiro Tomikawa<sup>4,5</sup>, and Nicholas B. Jones<sup>6</sup>

<sup>1</sup>National Institute for Environmental Studies, Tsukuba, Ibaraki, 305-8506, Japan
 <sup>2</sup>Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi, 980-8572, Japan
 <sup>3</sup>now at Weathernews Inc., Chiba, 261-0023, Japan
 <sup>4</sup>National Institute of Polar Research, Tachikawa, Tokyo, 190-8518, Japan
 <sup>5</sup>The Graduate University for Advanced Studies, Tachikawa, Tokyo, 190-8518, Japan
 <sup>6</sup>University of Wollongong, Wollongong, New South Wales, 2522, Australia

Correspondence to: Hideaki Nakajima (nakajima@nies.go.jp)

#### Abstract.

5

10

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 O<sub>3</sub>, HNO<sub>3</sub>, 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 CIO, HCl, and HNO<sub>3</sub> data taken with the Aura/MLS (Microwave Limb Sounder) satellite sensor, and CIONO<sub>2</sub> 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) existence temperature in early winter, PSCs started to form and heterogeneous reaction on PSCs convert chlorine reservoirs into reactive chemical species. HCl and CIONO<sub>2</sub> decrease occurred at both 18 and 22 km,
- and soon ClONO<sub>2</sub> was almost depleted in early winter. When the sun returned to Antarctica in spring, enhancement of ClO and gradual O<sub>3</sub> destruction were observed. During the ClO enhanced period, negative correlation between ClO and ClONO<sub>2</sub> 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. 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.
- 30 Rapid conversion of chlorine reservoir species (HCl and ClONO<sub>2</sub>) into Cl<sub>2</sub>, gradual conversion of Cl<sub>2</sub> into Cl<sub>2</sub>O<sub>2</sub>, 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 ClONO<sub>2</sub> from the subpolar region to higher latitudes,

providing a flux of  $CIONO_2$  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 airmass from lower latitudinal polar vortex boundary region which can produce additional  $CIONO_2$ by reaction of CIO with  $NO_2$ . The deactivation pathways from active chlorine into reservoir species (HCl and/or  $CIONO_2$ )

5 were found to be highly dependent on the availability of ambient O<sub>3</sub>. 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 O<sub>3</sub> available, additional increase of ClONO<sub>2</sub> from initial value can occur, similar to the case in the Arctic.

#### 1. Introduction

- 10 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 year-to-year variability. Although Solomon et al. (2016) and de
- 15 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  $(CIO_x=CI+CI_2+CIO+CIOO+CI_2O_2+HOCI+CINO_2)$  and chlorine reservoirs (HCl and CIONO\_2) are crucial. Chlorine reservoir is converted to active chlorine that destroys ozone on polar stratospheric clouds (PSCs) through heterogeneous reactions:

 $CIONO_{2}(g) + HCl(s, l) \rightarrow Cl_{2}(g) + HNO_{3}$ (R1)

$$CIONO_2(g) + H_2O(l, s) \rightarrow HOCl(g) + HNO_3$$
(R2)

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;

$$N_{2}O_{5}(g) + HCl(s, l) \rightarrow ClNO_{2}(g) + HNO_{3}$$
(R3)

30

$$HOCl (g) + HCl (s, l) \rightarrow Cl_2 (g) + H_2O$$
(R4)

are responsible for additional chlorine activation. When solar illumination is available,  $Cl_2$ , HOCl, and ClNO<sub>2</sub> are photolyzed to produce chlorine atoms by reactions:

$Cl_2 + hv \rightarrow Cl + Cl$	(R5)
$HOCl + hv \rightarrow Cl + OH$	(R6)
$ClNO_2 + hv \rightarrow Cl + NO_2.$	(R7)

The yielded chlorine atoms then start to destroy ozone catalytically through reactions:

$$Cl + O_3 \rightarrow ClO + O_2$$
 (R8)

$ClO + ClO + M \rightarrow Cl_2O_2 + M$	(R9)
$Cl_2O_2 + hv \rightarrow Cl + ClOO$	(R10)
$ClOO + M \rightarrow Cl + O_2 + M.$	(R11)

When the stratospheric temperatures get warmer than nitric acid trihydrate (NAT) PSC saturation temperature, and no PSCs
are present, gradual deactivation of chlorine starts to occur. Re-formation of ClONO<sub>2</sub> and HCl mainly occurs through reactions:

$$CIO + NO_2 + M \rightarrow CIONO_2 + M$$
(R12)

$$Cl + CH_4 \rightarrow HCl + CH_3.$$
 (R13)

The re-formation of ClONO<sub>2</sub> by reaction (R12) from active chlorine is much faster than that of HCl by reaction (R13), if there are enough NO<sub>x</sub> around (Mellqvist et al., 2002; Dufour et al., 2006). But the formation rates of ClONO<sub>2</sub> 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:

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{R14}$$

15 This makes NO/NO<sub>2</sub> ratio high and increases Cl/ClO ratio by the following reaction:

$$ClO + NO \rightarrow Cl + NO_2.$$
 (R15)

High Cl/ClO ratio leads rapid HCl formation by reaction (R13) and reduces the formation ratio of ClONO<sub>2</sub> by reaction (R12). 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 PSC formation threshold in the whole area of the polar vortex in

20 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 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

- 25 occur (Manney et al., 2011; WMO, 2014). In this case, some ozone, CIO, and NO<sub>2</sub> are available in the chlorine reservoir recovery phase. Therefore, the CIONO<sub>2</sub> 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 CIONO<sub>2</sub> than initial value at the time of chlorine deactivation in spring (Webster et al., 1993). In this way, the partitioning of chlorine reservoir in springtime is related to temperature, PSC amounts, ozone, and NO<sub>2</sub> concentrations (Santee et al., 2008; Solomon
- 30 et al., 2015).

In the polar regions, the ozone and related atmospheric trace gas species have been intensively monitored by several 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; 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

from the ground (e.g., Farmer et al., 1987; Kreher et al., 1996; 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. In this paper, we show the results of ground-based FTIR observations of O<sub>3</sub> and other trace gas species at Syowa

5 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<sub>x</sub>) and chlorine reservoirs (HCl, ClONO<sub>2</sub>) from fall to spring during 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, distributions of minor species simulated

10 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 highresolution FTIR site in Antarctica in operation after New Zealand's Arrival Heights facility at Scott Station (77.8°S, 166.7°E)

- 20 (Wood et al., 2002; Wood et al., 2004). The IFS-120M FTIR has a wavenumber resolution of 0.0035 cm<sup>-1</sup>, with two liquid nitrogen cooled detectors (InSb and HgCdTe covering the frequency ranges 2000-5000 and 700-1300 cm<sup>-1</sup>, 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 Julv).
- 25 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-
- 30 Interim reanalysis data.

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

5 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 O<sub>3</sub>, HCl, and HNO<sub>3</sub> 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<sub>3</sub>, monthly averaged profiles from ILAS-II for HNO<sub>3</sub> and monthly averaged profiles from HALOE (Anderson et al., 2000) for HCl. Typical averaging kernels of the SFIT2 retrievals for O<sub>3</sub>, HNO<sub>3</sub>, and HCl are shown in Figures 1(a), (b), and (c), respectively.

#### 15 **2.2 Satellite measurements**

20

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 HNO<sub>3</sub> 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<sup>-1</sup> (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
- 30 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. ClONO<sub>2</sub> 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 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

5 monitor aerosols, clouds, and polar stratospheric clouds (PSCs) (Pitts et al., 2007). CALIOP is a two-wavelength, polarization

15

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 PSCs over Syowa Station, we used CALIOP PSC data (Pitts et al., 2007; 2009; 2011).

#### 3. Validation of retrieved profiles from FTIR spectra with other measurements 10

We validated retrieved FTIR profiles of O<sub>3</sub> with ozonesondes, and HNO<sub>3</sub> 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  $\pm 6$  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)-(b) show absolute and percentage differences of  $O_3$  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).(1)

20 The absolute agreement between 15 and 25 km was within -0.02 to 0.40 ppmv. The relative difference D between 15 and 25 km was within -10.4 to +24.4%. The mean D of  $O_3$  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 2(c)-(d) show absolute and percentage differences of HNO<sub>3</sub> profiles retrieved by FTIR measurements and those from

- 25 Aura/MLS measurements, respectively, calculated from 44 coincident measurements. The agreement between 15 and 25 km was within -0.56 to +0.57 ppby. The D between 15 and 25 km was within -25.5 to +21.9%. The mean D for HNO<sub>3</sub> 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.
- 30 Figures 2(e)-(f) 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 ppby. The D between 15 and 25 km was within -34.1 to -3.0%. The mean 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%. 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.

5

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 3(a)-(d) show the time series of temperatures at 18 and 22 km over Syowa Station using ERA-Interim data (Dee et al.,

- 10 2011) for 2007 and 2011. Approximate saturation temperatures for NAT PSC ( $T_{NAT}$ ) and ice PSC ( $T_{ICE}$ ) calculated by assuming 6 ppbv HNO<sub>3</sub> and 4.5 ppmv H<sub>2</sub>O 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 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.
- 15 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 were sometimes below T<sub>NAT</sub> 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<sub>3</sub> (denitrification) and/or H<sub>2</sub>O 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<sub>2</sub>, ClO, Cl<sub>y</sub>\*, O<sub>3</sub>, and HNO<sub>3</sub> 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<sub>3</sub> (sonde) is observed with the KC96 ozonesonde for 2007 and the ECC-1Z ozonesonde for 2011 by JMA. HCl and HNO<sub>3</sub> observed by Aura/MLS are plotted to complement the data lack of FTIR measurements. ClONO<sub>2</sub> is observed by Envisat/MIPAS. Total inorganic chlorine Cl<sub>y</sub>\* corresponds to the sum of HCl, ClONO<sub>2</sub>, and Cl<sub>x</sub>, where active chlorine species Cl<sub>x</sub> is defined as the sum of ClO,
- 25 Cl, and 2\*Cl<sub>2</sub>O<sub>2</sub> (Bonne et al., 2000). Inferred total inorganic chlorine Cl<sub>y</sub>\* is calculated from N<sub>2</sub>O value (in ppbv) measured by MLS using the polynomial equation derived from the correlation of Cl<sub>y</sub> and N<sub>2</sub>O (Bonne et al., 2000):

 $Cl_{y}^{*}(pptv) = 4.7070^{*}10^{-7}(N_{2}O)^{4} - 3.2708^{*}10^{-4}(N_{2}O)^{3} + 4.0818^{*}10^{-2}(N_{2}O)^{2} - 4.6856(N_{2}O) + 3225.$  (2)

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:

30 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<sup>-1</sup>, see Nash et al. (1996) and Tomikawa et al. (2015)).

5

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 CIO and HCl (MLS) from day 195 to day 219, 2007 and CIONO<sub>2</sub>

10 from day 170 to day 216, 2007 (upper panels of Figures 4(a) and 6(a)) is due to large error in Aura/MLS or Envisat/MIPAS measurements during this period.

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

- 15 as follows: CIO 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 ClONO<sub>2</sub> decreased first, then ClO started to increase in winter, while HCl increases and ClO decreases were synchronized in spring. Cl<sub>y</sub>\* gradually increased in the polar vortex from late autumn to spring. The Cl<sub>y</sub>\* value became larger compared with its mixing ratio outside of the polar vortex in spring. O<sub>3</sub> decreased from
- 20 July to late September when ClO was present. HNO<sub>3</sub> showed large decreases from June to July, and then gradually increased in summer. Day-to-day variations of HNO<sub>3</sub> from June to August were large.

The following characteristics are evident especially at 18 km (Figures 4 and 5). The day-to-day variations of HCl from late June to early September were as small as 0-0.3 ppbv. The recovered values of HCl in spring were larger than those before winter and those outside the polar vortex during the same period. ClONO<sub>2</sub> kept near zero even after ClO disappeared, and did

not recover to the level before winter until spring.  $O_3$  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 following characteristics are evident only at 22 km (Figures 6 and 7). The day-to-day variation 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). ClONO<sub>2</sub> recovered to larger values than those before winter after ClO disappeared.

30 From winter to spring,  $O_3$  gradually decreased, but the magnitude of the decrease was much smaller than that at 18 km. As for the temporal increase of ClONO<sub>2</sub> 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 day 270, but we see no temporal increase of ClONO<sub>2</sub> at 18 km in 2007. Figure 7 shows that temporal ClO enhancement and decrease of O<sub>3</sub>, ClONO<sub>2</sub>, and HNO<sub>3</sub> occurred in early winter (day 150-

170) at 22 km in 2011. This small ozone depletion event before winter might be due to an airmass 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.

The ratios of observed HCl, ClONO<sub>2</sub>, 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:

5  $Cl_y (FTIR) = HCl (FTIR) + ClONO_2 (MIPAS) + ClO (MLS)$  (3)  $Cl_y (MLS) = HCl (MLS) + ClONO_2 (MIPAS) + ClO (MLS).$  (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. 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<sub>2</sub> was 0.2-0.3 before winter (day 130-140). The partitioning of HCl was three times larger than that of ClONO<sub>2</sub> at

- 10 that time. The ratio of CIO 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 CIONO<sub>2</sub> was 0-0.6 during this same period. CIONO<sub>2</sub> shows negative correlation with CIO, while HCl kept low even when CIO was low during this period. This negative correlation is shown in Figure 10 later. When CIO was enhanced, the O<sub>3</sub> amount gradually decreased, and finally reached <0.5 ppmv (>80% destruction) in October (day 280) (See Figures 4 and 5). The ratios became 0.9-1.0 for HCl and 0-0.1 for CIONO<sub>2</sub> after the recovery in spring (after day 290), indicating that
- 15 almost all chlorine reservoir species became HCl via reaction (R13), due to the lack of O<sub>3</sub> and NO<sub>2</sub> during this period. The ratios of Cl<sub>y</sub> (FTIR) and Cl<sub>y</sub> (MLS) were both around 0.7 at the time of ClO enhanced period (day 230-260). The remaining chlorine are thought to be Cl<sub>2</sub>O<sub>2</sub>, which will be shown in model simulation in Section 5 later. The ratio of Cl<sub>y</sub> became close to 1 after the recovery period (after day 280).

For both in 2007 and 2011 at 22 km (Figure 9), the ratio of HCl was 0.4-0.9 and the ratio of ClONO<sub>2</sub> was 0.2-0.3 before winter (day 110-140). The partitioning of HCl was two to three times larger than that of ClONO<sub>2</sub>. 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 ClONO<sub>2</sub> was 0-0.6 during this period. ClONO<sub>2</sub> shows negative correlation with ClO, while HCl kept low even when ClO was low during this period like the case at 18 km. The O<sub>3</sub> amount gradually decreased during the ClO enhanced period but remained >1.5 ppmv (less than half destruction) at this altitude (See Figures 6 and 7). When the ClO enhancement ended, temporal increase of ClONO<sub>2</sub>

- 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  $CIONO_2$  in spring (after day 280). This phenomenon shows that more chlorine deactivation via reaction (R12) occurred towards  $CIONO_2$  at 22 km rather than at 18km. 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 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  $Cl_2O_2$ . The ratio of  $Cl_y$  became around 1.1 after the
- 30 recovery period (after day 270). The reason why observed  $Cl_y$  values exceed calculated  $Cl_y^*$  values might be due to the difference in N<sub>2</sub>O-Cl<sub>y</sub> correlation at this altitude from the one in the equation (2).

In 2011 at 18 km (Figure 8), another temporal increase of  $CIONO_2$  up to a ratio of 0.6 occurred in early spring (around day 280) in accordance with HCl increase, then the  $CIONO_2$  amount gradually decreased to nearly zero after late October (day 300-). This temporal increase in  $CIONO_2$  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.  $O_3$  and HNO<sub>3</sub> showed higher values around day 280 (see Figure 5), indicating that Syowa Station was located close to the boundary region at this period. Therefore, the temporal increase of ClONO<sub>2</sub> in 2011 at 18 km was attributed to spatial variation, not to chemical evolution.

5

#### 5. Discussion

Figure 10 shows the correlation between ClO and ClONO<sub>2</sub> 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 ClONO<sub>2</sub>

- 10 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 ClO and ClONO<sub>2</sub> 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
- 15 vortex. When Syowa Station was located deep inside the polar vortex, there was more CIO and less CIONO<sub>2</sub>. On the contrary when Syowa Station was located near the vortex edge, there was less CIO and more CIONO<sub>2</sub>. 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.
- Figure 11 shows simulated mixing ratios of O<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, ClO, HCl, and ClONO<sub>2</sub> 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. 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 ClO, HCl, ClONO<sub>2</sub>, Cl<sub>y</sub>, and O<sub>3</sub> 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
- 25 CCM is discussed.

On June 24 (day 175), stratospheric temperatures over Antarctica were already low enough to allow PSCs to form. Consequently,  $NO_2$  and  $HNO_3$  in the polar vortex condensed onto PSCs. Note that the depleted area of  $NO_2$  was greater than that of  $HNO_3$ . This might be due to reaction (R12) that converts ClO and  $NO_2$  to ClONO<sub>2</sub> at the edge of the polar vortex, which is shown by the enhanced ClONO<sub>2</sub> area at the vortex edge in Figure 11. Also, HCl and ClONO<sub>2</sub> are depleted in the

30 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)

(ClONO<sub>2</sub>) was less than that of HCl (see Figure 4 and/or 5). The  $O_3$  amount was only slightly depleted within the polar vortex on this day.

On September 1 (day 244), amounts of NO<sub>2</sub>, HNO<sub>3</sub>, HCl, and ClONO<sub>2</sub> all show very depleted values in the polar vortex. The amount of ClO shows some enhanced values at the outer part of the polar vortex. Development of ozone depletion was seen

- 5 in the polar vortex. Note that ClONO<sub>2</sub> 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 ClO was smaller and ClONO<sub>2</sub> was greater than the values deep inside the polar vortex. On September 6 (day 249), 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 ClO was greater and ClONO<sub>2</sub> was smaller than the values around the boundary region of the polar vortex. Hence, the negative correlation between ClO and ClONO<sub>2</sub> seen in Figure 10 was due to variation of the relative distance between Syowa Station and the inner edge of the polar vortex.
- On October 6 (day 279), CIO enhancement has almost disappeared. Inside the polar vortex, O<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, and CIONO<sub>2</sub> 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 reaction (R13) deep inside the polar vortex,
- 15 where there is no  $O_3$  or  $NO_2$  left and reaction (R13) was favoured compared with reaction (R12). At Syowa Station, the amount of HCl was several times greater than that of ClONO<sub>2</sub> on this day.

Three-hourly time series of zonal-mean active chlorine species,  $Cl_2O_2$  (b),  $Cl_2$  (c), ClO (d), and their sum  $(ClO+2*Cl_2O_2+2*Cl_2)$  (a), and chlorine reservoir species HCl (e) and  $ClONO_2$  (f) modeled by MIROC3.2 CCM at 68.4°S, 71.2°S, 76.7°S, and 87.9°S are plotted in Figure 12. The dates on which the distribution of each species is shown in Figure 11

- 20 are indicated by vertical dotted lines. In this figure, it is shown that HCl and ClONO<sub>2</sub> rapidly decreased at around day 130 at 87.9°S, when PSCs started to form in the Antarctic polar vortex (Figures 12(e) and 12(f)). The decrease of HCl stopped when the counter-part of the heterogeneous reaction (R1) was missing at around day 140. Consequently, Cl<sub>2</sub> was formed (Figure 12(c)). Similar chlorine activation was seen at 76.7°S about 5-10 days later than at 87.9°S. Gradual conversion from Cl<sub>2</sub> into Cl<sub>2</sub>O<sub>2</sub> (ClO-dimer) was seen at all latitudes at around day 150-160 (Figures 12(b) and 12(c)) through reactions (R5), (R8), and
- (R9). At 87.9°S, conversion from Cl<sub>2</sub> to Cl<sub>2</sub>O<sub>2</sub> was slow, due to lack of sunlight which is needed for reaction (R5). Increase of ClO occurred much later in winter (day 190 or later), because sun light is needed to form ClO by reactions (R5) and (R8) in the polar vortex (Figure 12(d)). Nevertheless, there were some enhancements of ClO in early winter, day 175, simulated at the edge of the polar vortex (Figure 11) 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
- 30 day 255 (Figure 12(d)). Diurnal variation of CIO 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 3(a)), chlorine activation ended, and ClO was mainly converted into HCl at all latitudes inside the polar vortex (Figures 12(d) and 12(e)). This is because reaction (R13) occurs more frequently than reaction (R12) inside the polar vortex due to the depleted O<sub>3</sub> 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 12(e)). The cause of this continuous loss was unknown until recently, where a hypothesis was proposed that includes the effect of decomposition of particulate HNO<sub>3</sub> 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 new mechanism on this

5 issue: Continuous transport of CIONO<sub>2</sub> from the subpolar regions near 55-65°S to higher latitudes near 65-75°S provides a flux of NO<sub>x</sub> from more sunlit latitudes into the polar vortex. Our result also shows the same phenomena indicated by some sporadic increase in CIONO<sub>2</sub> at around days 158, 179, and 189 at 76.7°S as shown in Figure 12(f). Subsequently, HCl losses were observed at 76.7°S and 87.9°S during these episodes in Figure 12(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

10 strong.

#### 6. Conclusions

Lower stratospheric vertical profiles of O<sub>3</sub>, HNO<sub>3</sub>, and HCl were retrieved using SFIT2 from solar spectra taken with a groundbased FTIR installed at Syowa Station, Antarctica from March to December 2007 and September to November 2011. This

15 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 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

- 20 measurements of ClO, HCl, ClONO<sub>2</sub> and HNO<sub>3</sub>. When the stratospheric temperature over Syowa Station fell below PSC saturation temperature, PSCs started to form and heterogeneous reaction between HCl and ClONO<sub>2</sub> occurred and ClONO<sub>2</sub> was 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 O<sub>3</sub> destruction were observed. During the ClO enhanced period, negative correlation between ClO and ClONO<sub>2</sub> was observed in the time-series of the data at Syowa Station. This negative correlation is associated with
- 25 the 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. The modeled  $O_3$  and day-to-day variations of HCl and ClONO<sub>2</sub> are in good agreement with FTIR and satellite observations. Rapid conversion of chlorine reservoir species (HCl and ClONO<sub>2</sub>) into Cl<sub>2</sub>, gradual conversion of Cl<sub>2</sub> into Cl<sub>2</sub>O<sub>2</sub>, increase of ClO when sunlight became available, and conversion of ClO into

30 HCl were successfully reproduced by the CCM. HCl decrease in the winter polar vortex core continued to occur due to the transport of ClONO<sub>2</sub> from the subpolar region to higher latitudes, providing a flux of ClONO<sub>2</sub> 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 ClONO<sub>2</sub> by reaction (R12).

The deactivation pathways from active CIO into reservoir species (HCl and/or CIONO<sub>2</sub>) were found to be very dependent on the availability of ambient  $O_3$ . At an altitude (18 km) where most ozone was depleted in the Antarctic, most CIO was

5 converted to HCl. However, at an altitude (22 km) when there were some O<sub>3</sub> available, additional increase of ClONO<sub>2</sub> 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

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° × 2.8°) and 34 vertical atmospheric layers above the surface. The top layer is located at approximately 80 km

- 15 (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<sub>x</sub>, HO<sub>x</sub>, NO<sub>x</sub>, ClO<sub>x</sub>, BrO<sub>x</sub>, hydrocarbons for methane oxidation, heterogeneous reactions for sulfuric-acid aerosols, supercooled ternary solutions, nitric-acid trihydrate, and ice particles. The CCM contains
- 20 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.

#### Appendix B. Direct comparisons of mixing ratios of ClO, HCl, ClONO<sub>2</sub>, Cly, and O<sub>3</sub> 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, ClONO<sub>2</sub>, Cl<sub>y</sub>, and O<sub>3</sub> 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 these figures, Cl<sub>y</sub> by Aura/MLS represents the Cl<sub>y</sub>\* value defined by equation (2) using the N<sub>2</sub>O value measured by Aura/MLS.

30  $Cl_y$  from the MIROC3.2 CCM is the sum of total reactive chlorines, i.e.,  $Cl_y = Cl + 2*Cl_2 + ClO + 2*Cl_2O_2 + OClO + HCl + HOCl + ClONO_2 + ClNO_2 + BrCl.$ 

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 Cl<sub>2</sub>O<sub>2</sub> by reaction (R9) during nighttime. Also, modeled HCl and Cl<sub>y</sub> 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 airmass

5 across the subtropical barrier in MIROC3.2 CCM (Akiyoshi et al., 2016). Nevertheless, day-to-day relative variations of measured HCl and ClONO<sub>2</sub> are fairly well reproduced by the MIROC3.2 CCM. Modeled O<sub>3</sub> were in very good agreement with FTIR and/or MLS measurements throughout the year in both altitudes for both years.

#### Acknowledgments

- 10 We acknowledge Dr. Takeshi Kinase for making the FTIR observation at Syowa Station in 2011. All the members of the 48<sup>th</sup> Japanese Antarctic Research Expedition (JARE-48), JARE-52 are acknowledged for their support in making the FTIR observation at Syowa Station. Data provision of Aura/MLS and Envisat/MIPAS are much appreciated. We thank Japan Meteorological Agency for providing the ozonesonde and Rawin sonde data at Syowa Station. Thanks are due to Dr. Yosuke Yamashita for performing the CCM run and Dr. Eric Dupuy for preparing figures of the model output. The model
- 15 computations were performed on NEC-SX9/A(ECO) and NEC SX-ACE computers at the CGER, NIES, supported by the Environment Research and Technology Development Funds of the Ministry of the Environment (2-1303) and Environment Restoration and Conservation Agency (2-1709). We thank Dr. Takafumi Sugita for useful discussion and comments.

#### References

25

- 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, 10.1029/1999jd901075, 2000.
  - 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
- 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.

CCMVal scenarios, J. Geophys. Res., 114, D03103(1-28), doi:10.1029/2007JD009261, 2009.

30 Akiyoshi, H., Nakamura, T., Miyasaka, T., Shiotani, M., and Suzuki, M.: A nudged chemistry-climate model simulation of 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-O<sub>3</sub> anticorrelation based on in situ ER-2 data, J. Geophys. Res., 94, 11,465-11479, 1989.
- Anderson, J., Russell, J. M., III, Solomon, S., and Deaver, L. E.: Halogen Occultation Experiment confirmation of stratospheric
- 5 chlorine decreases in accordance with the Montreal Protocol, J. Geophys. Res., 105, 4483-4490, 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.
- 10 Bonne, G. P., Stimpf1le, 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.
- 15 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.
- 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.
  - 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.
   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 ClONO<sub>2</sub> in the polar vortices, J. Geophys. Res., 100, 13,967-13,978, 1995.
- 30 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 ClONO<sub>2</sub> 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 ClOx/NOx interaction, Nature, 315, 207-210, 1985.

- Farmer, C. B., Toon, G. C., Schaper, P. W., Blavier, J. -F., and Lowes, L. L.: Stratospheic 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.
- 5 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.
  - 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.
- 10 Grooß, J. -U., Brautzsch, 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.
  - Grooß, 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,
- 15 doi:10.5194/acp-18-8647-2018, 2018
  - 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 ClONO<sub>2</sub> observed with Improved Limb
- 20 Atmospheric Spectrometer (ILAS) during Arctic late winter and early spring in 1997, J. Geophys. Res., 112, D14311, doi:10.1029/2006JD008108, 2007.
  - 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 ClONO<sub>2</sub> 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
- 30 of MIPAS ClONO<sub>2</sub> measurements, Atmos. Chem. Phys., 7, 257-281, 2007.
  - 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.

- 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.
- Kuttippurath, J., Goutail, F., Pommereau, J. -P., Lefèvre, F., Roscoe, H. K., Pazmiñno, 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.
- 5
  - 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.
- 10 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.
  - 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
- der Gathen, P., Walker, K. A., and Zinoviev, N. S.: Unprecedented Arctic ozone loss in 2011. Nature, 478, 469-475. 15 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., Yashcov, 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, 10.1029/2001JD001080, 2002. 20
  - 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 Spivakovssky, C. M.: Maintenance of high HCl/Cl<sub>y</sub> and NO<sub>y</sub>/NO<sub>y</sub> in the Antarctic vortex: A chemical signature of confinement during spring, J. Geophys.. Res., 104, 26,419-26,436, 1999.
    - Müller, R., Crutzen, P. J., Grooß, J. -U., Brühl, C., Russell III, J. M., and Tuck, A. F.: Chlorine activation and ozone
- 25 depletion in the Arctic vortex: Observations by the Halogen Occultation Experiment on the Upper Atmosphere Research Satellite, J. Geophys. Res., 101, D7, 12,531-12,554, 1996.
  - 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,

30 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.

- 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.
- Norton, R., and Rinsland, C.: ATMOS data processing and science analysis methods, Appl. Opt., 30, 389-400, 1991.

- 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, 2007.
- 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, 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, 2011.
- 15 Rees, D., Barnett, J. J., and Labitske, K.: COSPAR International Reference Atmosphere: 1986, Part II, Middle Atmosphere Models, Adv. Space Res., 10, 1-525, 1990.
  - 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.
   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, 10.1029/2005JD006315, 2006.
- 25 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. 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
- 30 stratosphere from UARS Microwave Limb Sounder measurements, J. Geophys.. Res., 108, D15, 4454, 10.1029/2002JD003335, 2003.
  - 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, 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 lowermost stratosphere from Aura Microwave Limb Sounder measurements, J. Geophys. Res., 116, D18306, 10.1029/2011jd015590, 2011.
- 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., 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., Kinninson, D., Mills, M. J., Neely III, R. R., and Schmidt, A.: Emergene of healing in the Antarctic ozone layer, Science, doi:10.1126/science.aae0061, 2016.
- 10 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.
  - 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.,
- 15 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 mesosphere measured by the Improved Limb Atmospheric Spectrometer (ILAS)-II: Comparison with other satellite sensors and ozonesondes, J. Geophys. Res., 111, D11S02, 10.1029/2005jd006439, 2006.
  - Tomikawa, Y., and Sato, K.: Trapped waves in the edge region of stratospheric polar vortices, J. Geophys. Res., 108, 4047,

20 http://dx.doi.org/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.
- 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.
  - 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.
  - Webster, C. R., May, R. D., Toohey, D. W., Avallone, L. M., Anderson, J. G., Newman, P., Lait, L., Schoeberl, M. R., Elkins,
- 30 J. W., and Chan, K. R.: Chlorine chemistry on polar stratospheric cloud particles in the Arctic winter, Science, 261, 1130-1134, 1993.
  - 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, 516 pp., Geneva, Switzerland, 2011.
- 5 WMO: Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project—Report No. 55, 416 pp., Geneva, Switzerland, 2014.
  - 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 HNO<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, O<sub>3</sub>, and NO<sub>2</sub> using ground-based measurements at Arrival Heights and Kiruna, J. Geophys. Res., 107, 8208, 10.1029/2001jd000581, 2002.
- 10 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, 10.1029/2004jd004665, 2004.
  - 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, 10.1029/2007JD009675, 2008.
- 15 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, 10.5194/acp-11-9237-2011, 2011.

## Tables

Month	Dates	Dates	Number of days	Number of days	Number of days	Number of
	(2007)	(2011)	vortex	region of the	vortex	days
			(2007/2011)	polar vortex	(2007/2011)	(2007/2011)
				(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,	25, 29, 30	12/3	0 / 0	0 / 0	12/3
	27, 30					
October	6, 10, 11, 14, 19, 20, 25, 26, 27	1, 3, 4, 8, 11, 22, 23,	9 / 9	0 / 0	0 / 0	9 / 9
		24, 26				
November	2, 3, 5, 6, 7, 8, 9, 10, 11, 16,	1, 2, 3, 9, 11, 16, 19	12 / 7	1 / 0	4 / 0	17 / 7
	17, 18, 19, 21, 27, 29, 30					
December	4, 7, 8, 9, 13, 15, 16, 17, 20,		8 / 0	0 / 0	3 / 0	11 / 0
	22, 29					
Total			56 / 19	4 / 0	18 / 0	78 / 19

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

Species	$O_3$	HNO <sub>3</sub>	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 <sup>-1</sup> )	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 <sub>3</sub> (668), O <sub>3</sub> (686), CO <sub>2</sub> , H <sub>2</sub> O	H <sub>2</sub> O, OCS, NH <sub>3</sub> , CO <sub>2</sub> , C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub> , H <sub>2</sub> O, O <sub>3</sub> , NO <sub>2</sub>	

## Table 2. Retrieval parameters of SFIT2

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

	D (%) 18-22 km	Min/Max (%) 18-22 km	Agreement 15-25 km (ppmv/ppbv)	Literature values
<b>O</b> <sub>3</sub>	+6.2	-10.4/+19.2	-0.02~+0.40	
HNO <sub>3</sub>	+13.2	+0.2/+21.9	-0.56~+0.57	Aura/MLS no bias with errors (0.6 ppbv) (Livesey et al., 2011)
HCI	-9.7	-14.6/-3.0	-0.2~+0.09	Aura/MLS > HALOE by 10-15%, precision 0.2-0.6 ppbv (Livesey et al., 2013)

## Table 4. Summary of minor atmospheric species variations

Altitude	18 km		22 km	
Year	2007	2011	2007	2011
Period of enhanced ClO (day)	230-260	230-260	220-240	230-250
Variation when ClO 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
ClONO <sub>2</sub> Value before winter (ppbv)	~0.5	~0.4	0.6–0.9	0.6–0.7
Variation when ClONO <sub>2</sub> ~0 (ppbv)	0–1.5	0–1.5	0–2.0	0–2.0
Day of CIONO <sub>2</sub> enhancement	-	270-300	270-280	270–280
Value of ClONO <sub>2</sub> enhancement (ppbv)	-	1.5	1.5	1.5
ClONO <sub>2</sub> value after enhancement (ppbv)	0–0.3	0-0.2	0.8–1.3	0.8–1.1
CIONO <sub>2</sub> value outside polar vortex (ppbv)	0.3–0.4	0.2–0.3	0.5–0.7	0.6–0.8
O <sub>3</sub> value before winter (ppmv)	2.5	2.5	4.0	4.0
O <sub>3</sub> starting-ending day of decrease (day)	190-280	200-270	170-260	170-270
O <sub>3</sub> minimum value (ppmv)	0.3	0.5	2.0	1.0
O <sub>3</sub> value after recovery (ppmv)	0.8	0.8	2.4-4.0	2.0–3.5
HNO <sub>3</sub> value before winter (ppbv)	6-10	8-10	15-16	13–15
HNO3 starting-ending day of decrease (day)	160-190	150-180	140-180	150-180
HNO <sub>3</sub> minimum value (ppbv)	0	0	2	1
HNO <sub>3</sub> value after recovery (ppbv)	3–4	3–4	4–6	4–5



Figure 1. Averaging kernel functions of the SFIT2 retrievals for O<sub>3</sub> (a), HNO<sub>3</sub> (b), and HCl (c).



Figure 2. Absolute (a) and percentage (b) differences of  $O_3$  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 HNO<sub>3</sub> 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 3. Time series 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<sub>3</sub> and 4.5 ppmv H<sub>2</sub>O 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, ClONO<sub>2</sub>, ClO,  $Cl_y^*$ , (b) O<sub>3</sub>, and HNO<sub>3</sub> mixing ratios at 18 km in 2007 over Syowa Station. O<sub>3</sub>(FTIR), HCl(FTIR), and HNO<sub>3</sub>(FTIR) were measured by FTIR at Syowa Station, while HCl(MLS), ClO, and HNO<sub>3</sub>(MLS) were measured by Aura/MLS. O<sub>3</sub>(sonde) was measured by ozonesonde. ClONO<sub>2</sub> was measured by Envisat/MIPAS.  $Cl_y^*$  is calculated from N<sub>2</sub>O value. See text in detail. The unit of O<sub>3</sub> 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 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, ClONO<sub>2</sub>, ClO, and  $Cl_y$ (=HCl+ClONO<sub>2</sub>+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 4.



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



Figure 10. Scatter plot between ClO (Aura/MLS) and ClONO<sub>2</sub> (Envisat/MIPAS) mixing ratios between August 8 and September 17 (day 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 11. Polar southern hemispheric plot for simulated mixing ratios of O<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, ClO, HCl, and ClONO<sub>2</sub> 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 12. Three-hourly zonal-mean time series of MIROC3.2 CCM outputs for (a)  $ClO+2*Cl_2O_2+2*Cl_2$ , (b)  $Cl_2O_2$ , (c)  $Cl_2$ , (d) ClO, (e) HCl, and (d)  $ClONO_2$  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 ClO, B1(b) is for HCl, B1(c) is for ClONO<sub>2</sub>, B1(d) is for Cly, and B1(e) is for O<sub>3</sub> in 2007. Figure B1(f) is for ClO, B1(g) is for HCl, B1(h) is for ClONO<sub>2</sub>, B1(i) is for Cly, and B1(j) is for O<sub>3</sub> in 2011.



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