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

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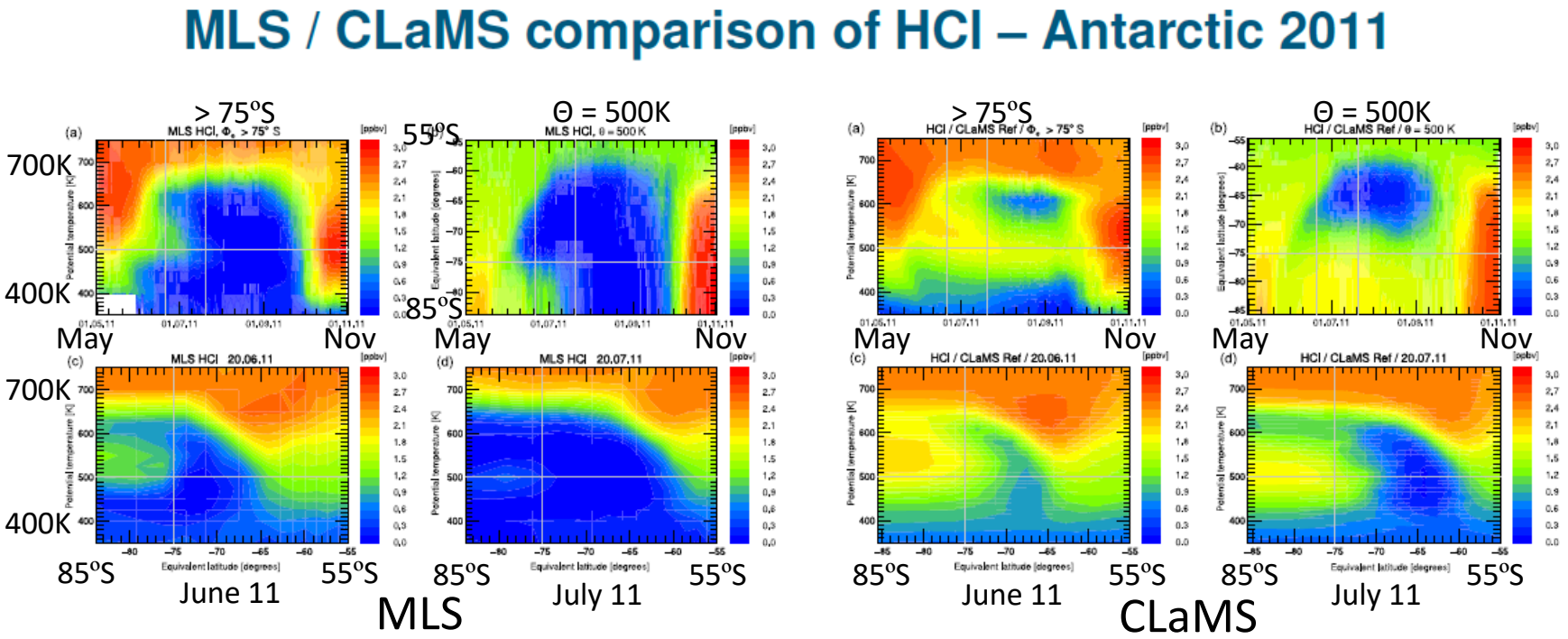
NIES

# Unsolved Question (1) HCl Discrepancy

- Heterogenous reaction: $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ stops in the core of polar vortex.
- During winter in the polar vortex, HCl continues to decrease @500K in MLS, But, models (CLaMS, SD-WACCM, TOMCAT/SLIMCAT) cannot reproduce it.




[Grooß et al., ACP, 2018]

# Unsolved Question (2) HCl null cycles

- Maintenance of elevated active chlorine levels in Antarctic spring by two HCl null cycles.
- Missing pathway to decrease in HCl in early July to late August, especially when solar illumination is not available.

## HCl null cycle (C1)

$$\mathrm{CH_4 + Cl \rightarrow HCl + CH_3}, \quad (R4)$$
$$\mathrm{CH_3 + O_2 + M \rightarrow CH_3O_2 + M}, \quad (R5)$$
$$\mathrm{CH_3O_2 + ClO \rightarrow CH_3O + Cl + O_2}, \quad (R3)$$
$$\mathrm{CH_3O + O_2 \rightarrow HO_2 + CH_2O}, \quad (R6)$$
$$\mathrm{ClO + HO_2 \rightarrow HOCl + O_2}, \quad (R7)$$
$$\mathrm{HOCl + HCl \rightarrow Cl_2 + H_2O}, \quad (R2)$$
$$\mathrm{Cl_2 + h\nu \rightarrow 2Cl}, \quad (R8)$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2} \quad (2\times), \quad (R9)$$
$$\text{Net(C1)}: \quad \mathrm{CH_4 + 2O_3 \rightarrow CH_2O + H_2O + 2O_2}. \quad (R10)$$

## HCl null cycle (C2)

$$\mathrm{CH_2O + Cl \rightarrow HCl + CHO} \quad (R11)$$
$$\mathrm{CHO + O_2 \rightarrow CO + HO_2} \quad (R12)$$
$$\mathrm{ClO + HO_2 \rightarrow HOCl + O_2} \quad (R7)$$
$$\mathrm{HOCl + HCl \rightarrow Cl_2 + H_2O} \quad (R2)$$
$$\mathrm{Cl_2 + h\nu \rightarrow 2Cl} \quad (R8)$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2} \quad (R9)$$
$$\text{Net(C2)}: \quad \mathrm{CH_2O + O_3 \rightarrow CO + H_2O + O_2} \quad (R13)$$

## HCl delete cycle (C3)

$$\mathrm{CH_2O + h\nu \rightarrow CHO + H}, \quad (R14)$$
$$\mathrm{H + O_2 + M \rightarrow HO_2 + M}, \quad (R15)$$
$$\mathrm{CHO + O_2 \rightarrow CO + HO_2}, \quad (R12)$$
$$\mathrm{ClO + HO_2 \rightarrow HOCl + O_2} \quad (2\times), \quad (R7)$$
$$\mathrm{HOCl + HCl \rightarrow Cl_2 + H_2O} \quad (2\times), \quad (R2)$$
$$\mathrm{Cl_2 + h\nu \rightarrow 2Cl} \quad (2\times), \quad (R8)$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2} \quad (4\times), \quad (R9)$$
$$\text{Net(C3)}: \quad \mathrm{CH_2O + 2HCl + 4O_3 \rightarrow CO + 2ClO + 2H_2O + 4O_2}, \quad (R16)$$

## HCl delete cycle (C4)

$$\mathrm{O_3 + h\nu \rightarrow O(^1D) + O_2}, \quad (R17)$$
$$\mathrm{O(^1D) + H_2O \rightarrow 2OH}, \quad (R18)$$
$$\mathrm{OH + O_3 \rightarrow HO_2 + O_2} \quad (2\times), \quad (R19)$$
$$\mathrm{ClO + HO_2 \rightarrow HOCl + O_2} \quad (2\times), \quad (R7)$$
$$\mathrm{HOCl + HCl \rightarrow Cl_2 + H_2O} \quad (2\times), \quad (R2)$$
$$\mathrm{Cl_2 + h\nu \rightarrow 2Cl} \quad (2\times), \quad (R8)$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2} \quad (4\times), \quad (R9)$$
$$\text{Net(C4)}: \quad \mathrm{2HCl + 7O_3 \rightarrow 2ClO + H_2O + 9O_2}. \quad (R20)$$

Reaction (R19) may also proceed in two steps:

$$\mathrm{OH + ClO \rightarrow HO_2 + Cl}, \quad (R21)$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2}, \quad (R9)$$
$$\text{Net}: \quad \mathrm{OH + O_3 \rightarrow HO_2 + O_2}.$$

[Müller et al., ACP, 2018]

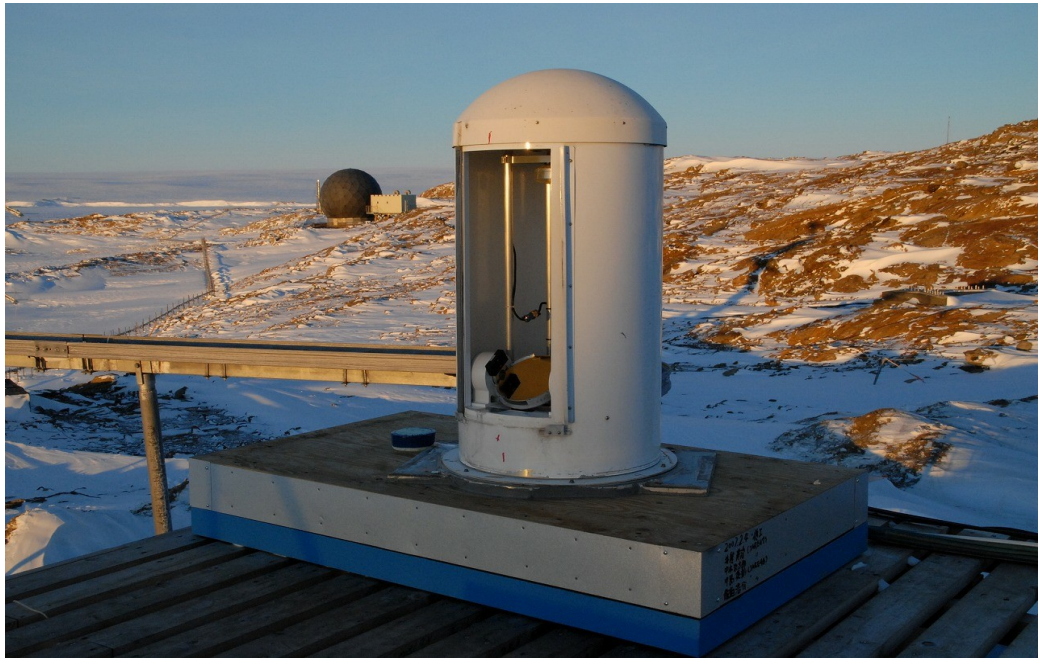
# Purpose of This Study

- To study Antarctic chlorine partitioning (especially continuous HCl loss in polar vortex) in winter/spring

  For that purpose,

- We used ground-based FTIR data at Syowa Station (69˚S, 39˚E)
- In addition, we used satellite data by Aura/MLS and Envisat/MIPAS
- We compared our results with MIROC3.2 CCM results
- Study temporal variation of chlorine species in 2007 and 2011

# Installation of FTIR Spectrometer at Syowa Station, Antarctica (69°S, 39°E) in 2007



A sun-tracker installed on the roof of observation hut at Syowa Station

FTIR observation at Syowa Station

# Number of FTIR Measurements at Syowa

**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 at the edge 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 |

FTIR Observations
At Syowa Station

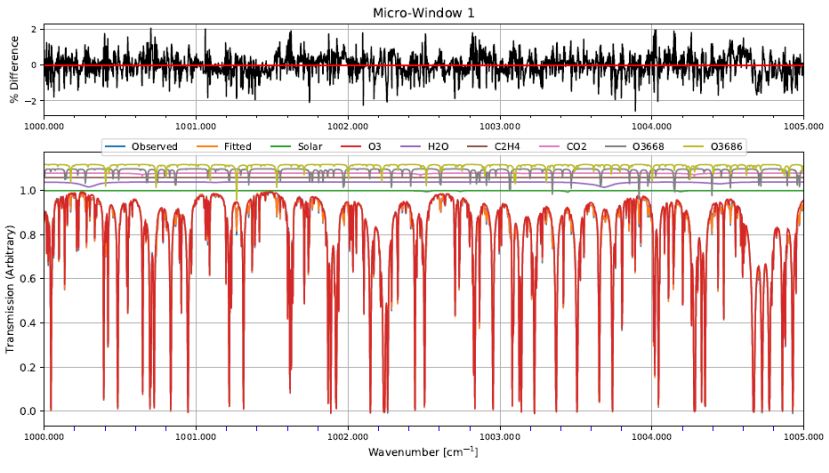
78 days (2007)
19 days (2011)

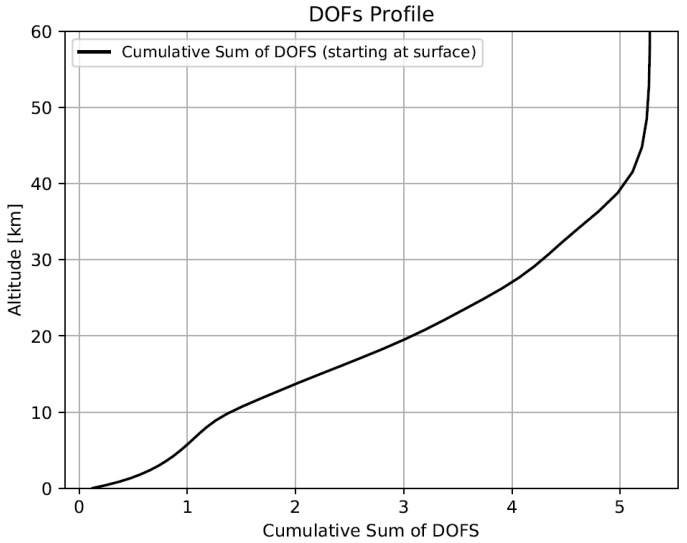
# FTIR Retrieval Parameters

**Table 2. Retrieval parameters**

| Species | $O_3$ | $HNO_3$ | HCl |
|---|---|---|---|
| **Spectroscopy** | HITRAN 2008 | HITRAN 2008 | HITRAN 2008 |
| **PT Profile** | Daily sonde (0-30 km)<br>CIRA 86 (30-100 km) | Daily sonde (0-30 km)<br>CIRA 86 (30-100 km) | Daily sonde (0-30 km)<br>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<br>1003.900 – 1004.400<br>1004.578 – 1005.000 | 867.000 – 869.591<br>872.800 – 874.000 | 2727.730 – 2727.830<br>2775.700 – 2775.800<br>2925.800 – 2926.000 |
| **Retrieved interfering species** | $O_3$ (668), $O_3$ (686), $CO_2$, $H_2O$ | $H_2O$, OCS, $NH_3$, $CO_2$, $C_2H_6$ | $CO_2$, $H_2O$, $O_3$, $NO_2$ |

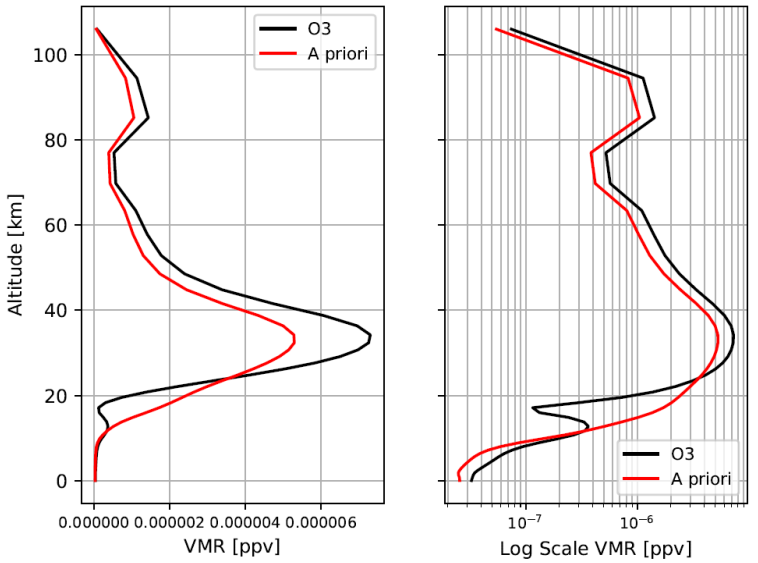
# Retrieved $O_3$ Profile on October 11, 2007 over Syowa

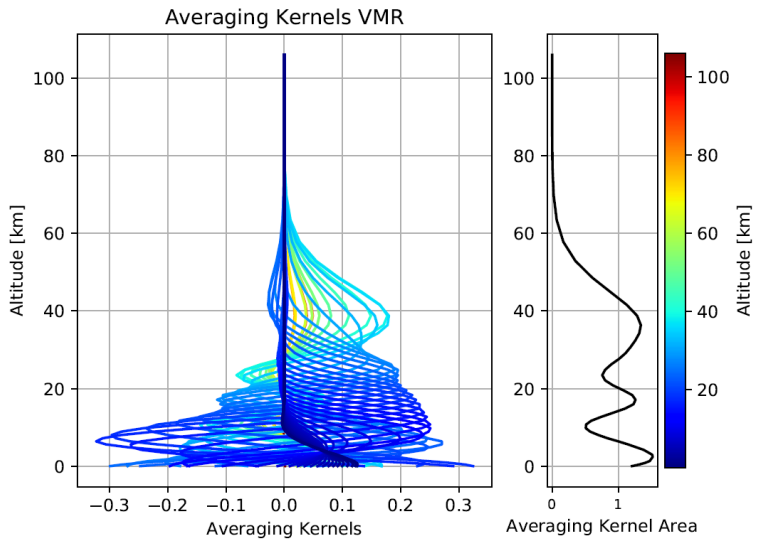



Number of Obs Filtered = 0
Number of Obs After Filtering = 1

O3



# Averaging Kernel Functions

$O_3$ $HNO_3$ HCl

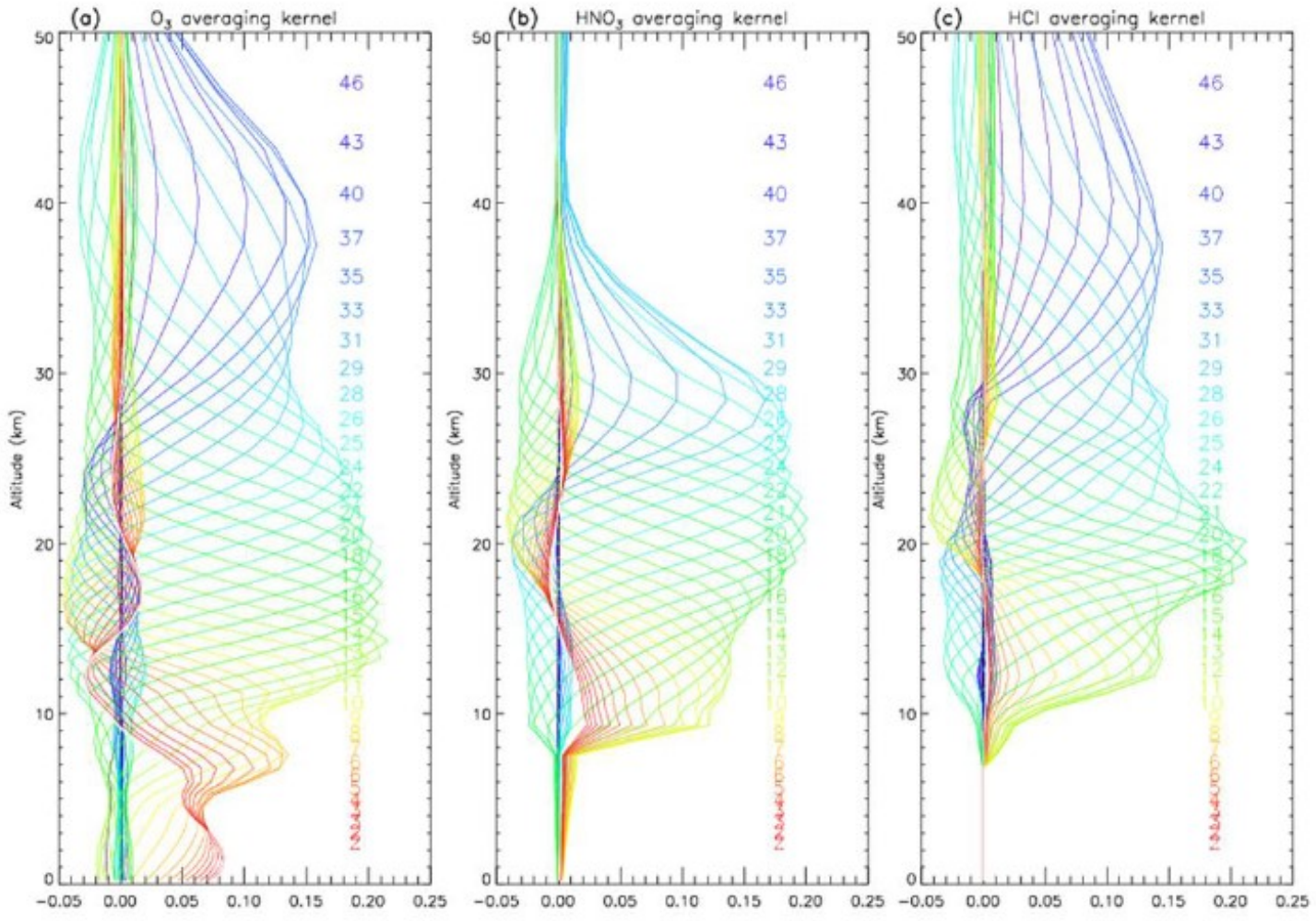



**Figure 1.** Averaging kernel functions of the SFIT2 retrievals for (**a**) $O_3$, (**b**) $HNO_3$, and (**c**) HCl.

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# Variation of Temperatures over Syowa

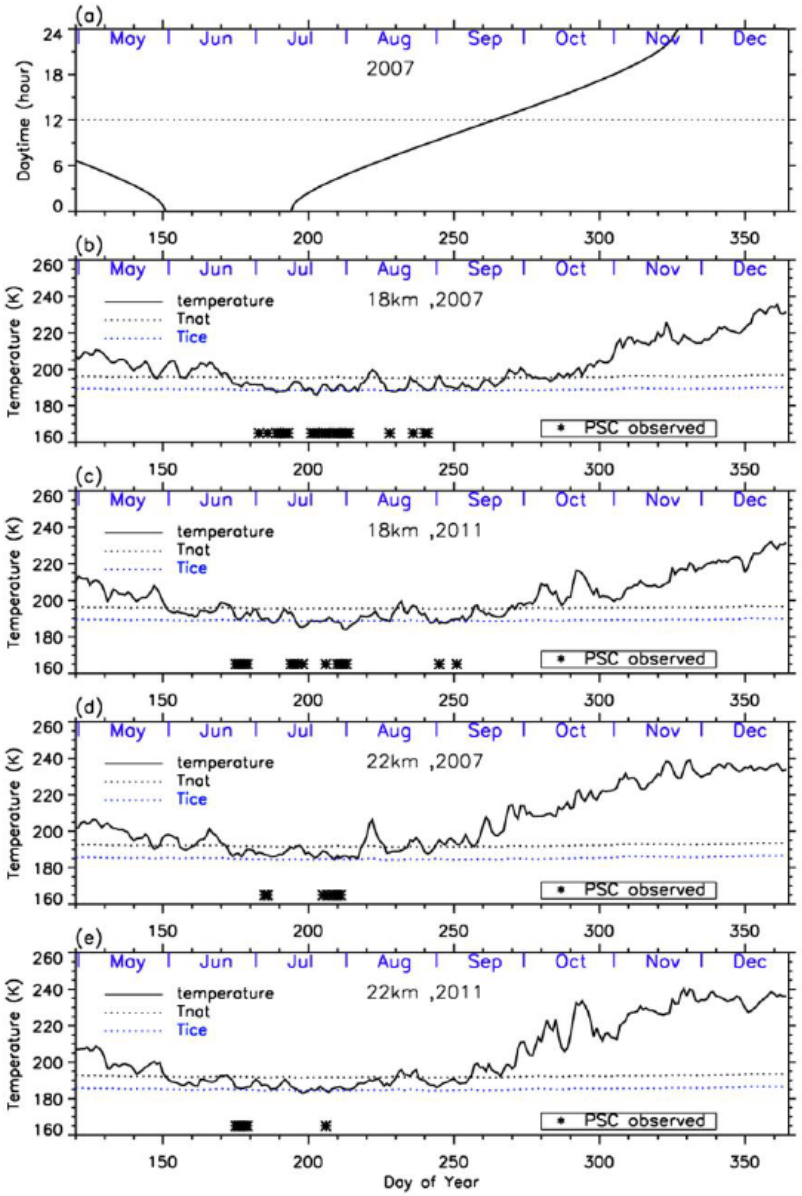


**Figure 3.** Time series of **(a)** daytime hour and temperatures at 18 km in **(b)** 2007 and **(c)** 2011 and at 22 km in **(d)** 2007 and **(e)** 2011 over Syowa Station using ERA-Interim data. Approximate saturation temperatures for nitric acid trihydrate ($T_{NAT}$) and ice ($T_{ICE}$) calculated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

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# Variation of Minor Species over Syowa (18 km) in 2007

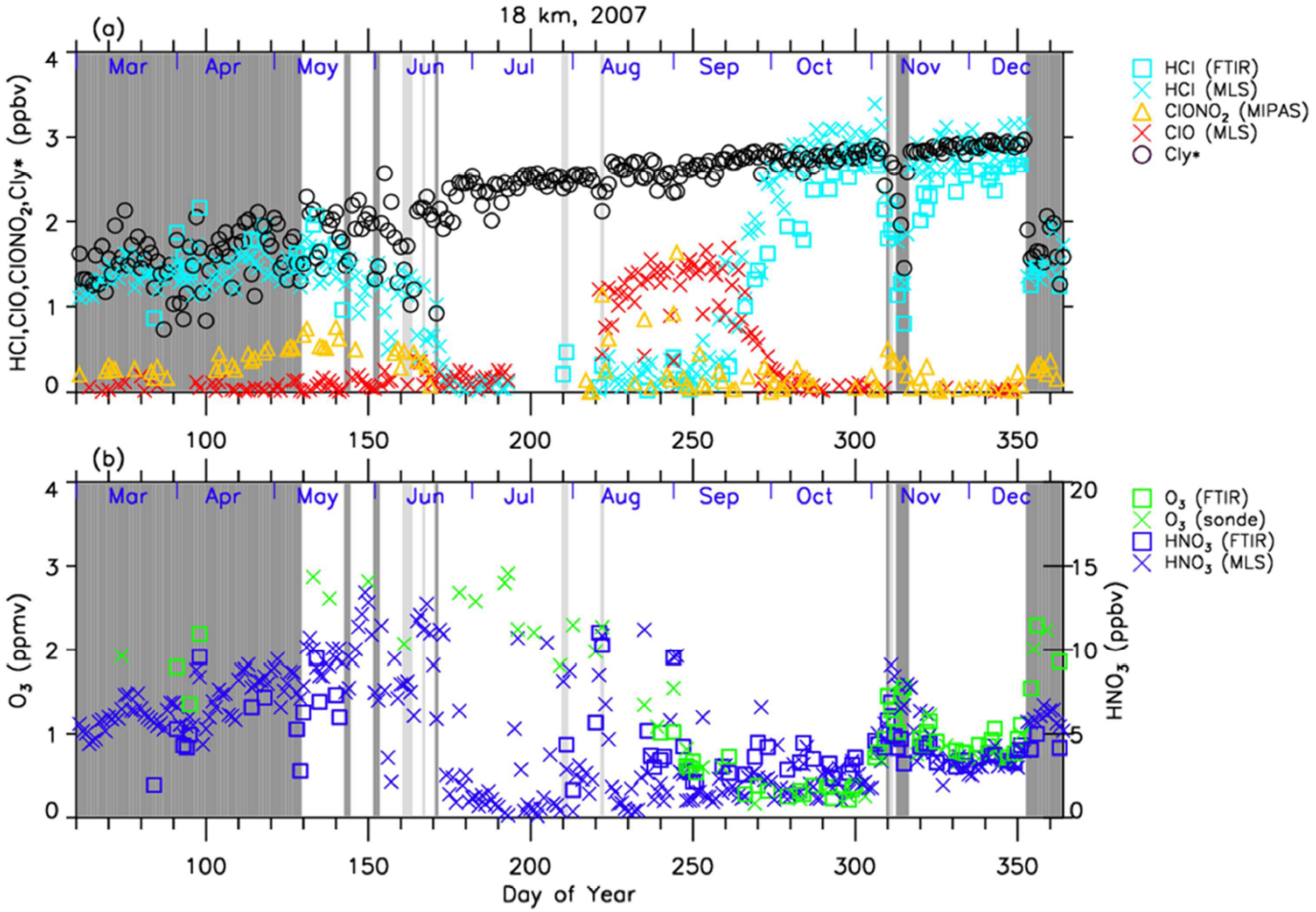


**Figure 4.** Time series of **(a)** HCl, $ClONO_2$, ClO, and $Cl_y^*$ as well as **(b)** $O_3$ and and $HNO_3$ mixing ratios at 18 km in 2007 over Syowa Station. $O_3$(FTIR), HCl(FTIR), and $HNO_3$(FTIR) were measured by FTIR at Syowa Station, while HCl(MLS), ClO(MLS), and $HNO_3$(MLS) were measured by Aura MLS. $O_3$(sonde) was measured by ozonesonde. $ClONO_2$ was measured by Envisat MIPAS. $Cl_y^*$ is calculated from the Aura MLS $N_2O$ value. See text in detail. The unit of $O_3$ is parts per million by volume (ppmv) and the other gases are parts per billion by volume (ppbv). The dark shaded area, the light shaded area, and the white area indicate the days when Syowa Station was located outside the polar vortex, in the boundary region of the polar vortex, and inside the polar vortex, respectively.

- ClO enhancement from Aug. to Sep.
- HCl and $ClONO_2$ depleted to nearly zero from Jun. to beg. Sep.
- Cly* increased from fall to spring
- $O_3$ started to decrease from July to end Sep.
- $HNO_3$ suddenly decreased in Jul.
- In mid-winter (Jul), all HCl, $ClONO_2$, and ClO were zero.
- In spring (Aug-Sep), $ClONO_2$↑& ClO↓ anti-correlated sometimes.

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# Variation of Minor Species over Syowa (22 km) in 2007

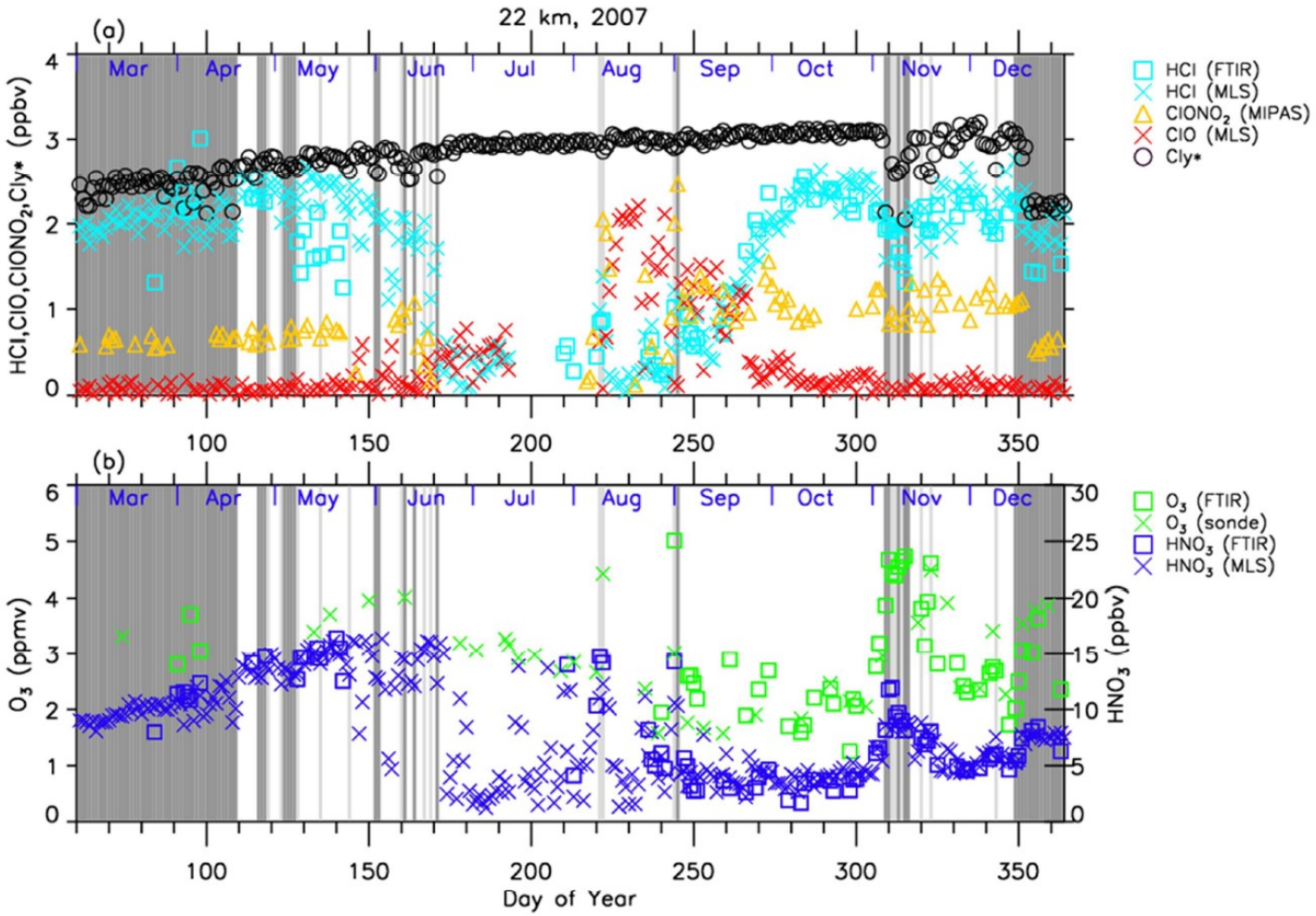


**Figure 6.** Same as Fig. 4 but at 22 km.

<Difference in 22 km compared with 18 km>

- $ClONO_2$ returned to greater values (super-recovery) after spring (Sep-Nov) than previous values before winter (May-Jun).
- $ClONO_2$ anti-correlation with ClO was more often seen during spring (Aug.-Sep.)
- $O_3$ was not completely destroyed in spring at this altitude.

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# Variation of Minor Species over Syowa (22 km) in 2011

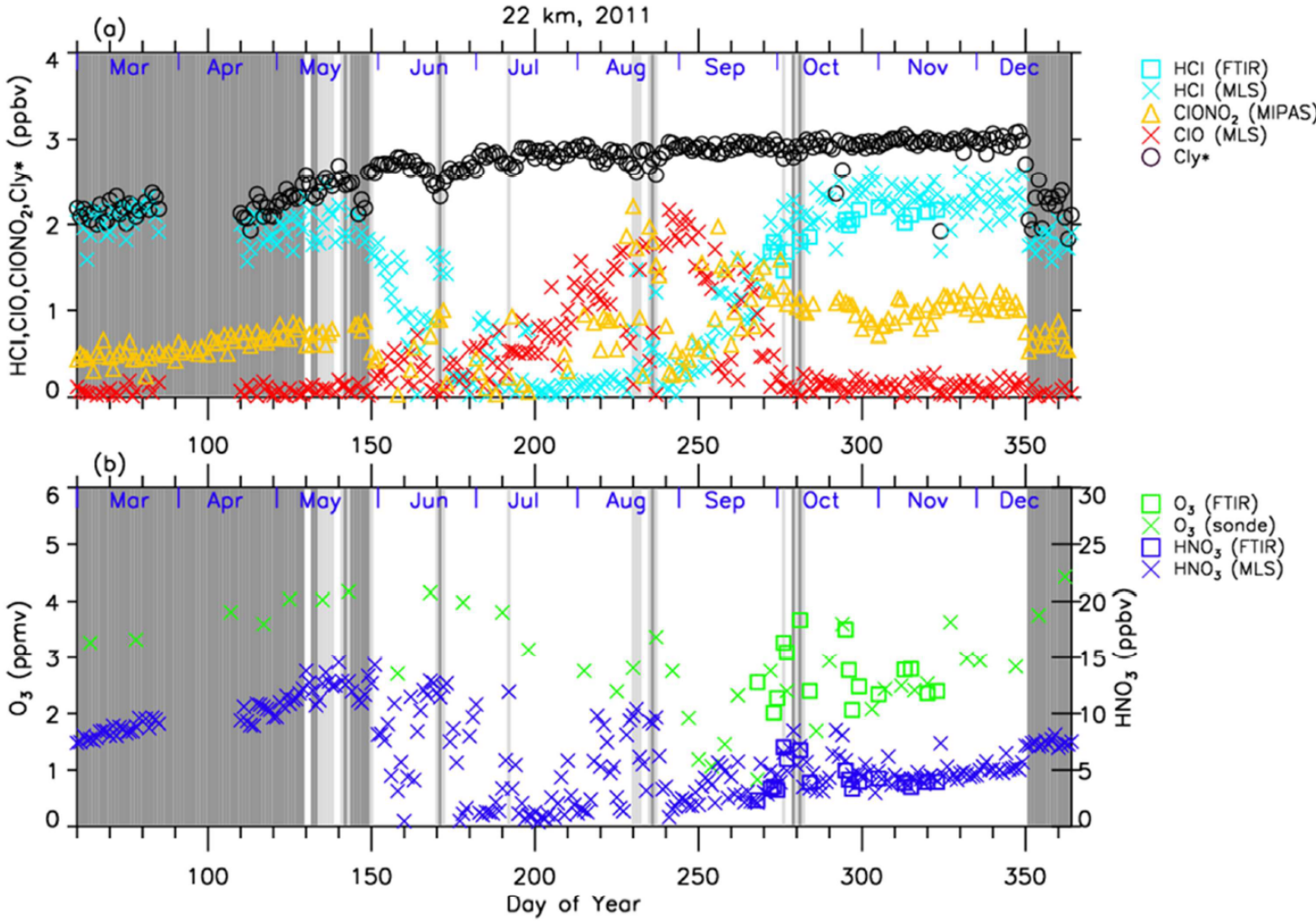


**Figure 7.** Same as Fig. 5 but at 22 km.

<Difference in 2011 22 km compared with 2007 22 km>

- Early ClO enhancement/HCl decrease was seen in early June (Day 150-170), before the sighting of PSC over Syowa Station → suggesting early chlorine activation
- Early $O_3$ depletion was seen at Day 158

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# Ratios of Chlorine Species over Syowa (18 km)

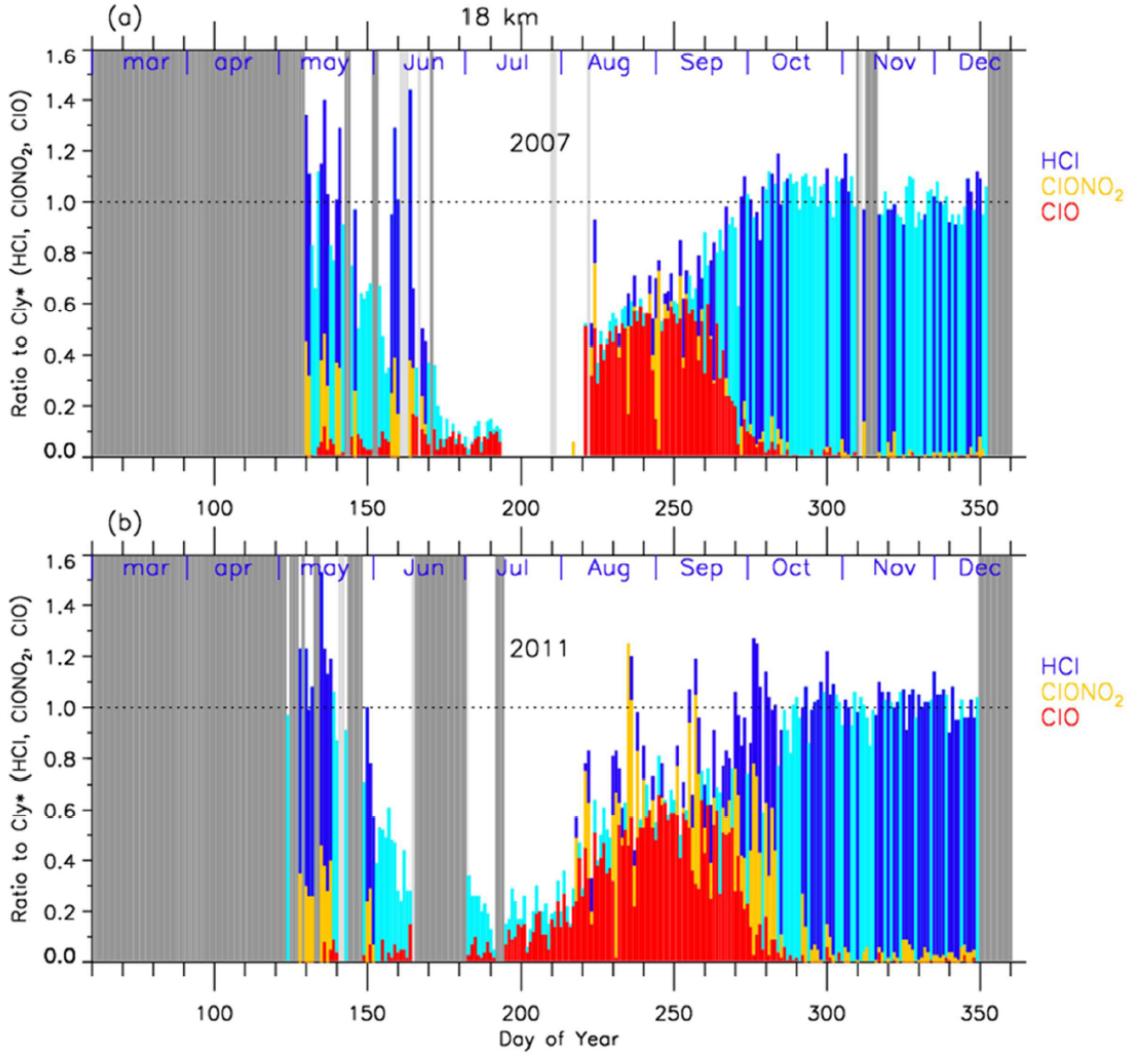


**Figure 8.** Time series of the ratios of HCl (dark blue or light blue), $ClONO_2$ (yellow), and ClO (red) to total chlorine ($Cl_y^*$) over Syowa Station at 18 km in **(a)** 2007 and in **(b)** 2011. Light blue shows that either $ClONO_2$ or ClO data were missing on that day, while dark blue shows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

- Before winter, HCl:$ClONO_2$ ratio is ~2:1
- From June, HCl and $ClONO_2$ gradually depleted to nearly zero from in July.
- After sunlight come back to Syowa Station in late July , active ClO increased.
- Missing Cly species might be eigher $Cl_2O_2$ , or HOCl.
- After mid September, ClO amount started to decrease, due to deactivation.
- Most Cly were converted into HCl at this altitude (18 km).

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# Ratios of Chlorine Species over Syowa (22 km)

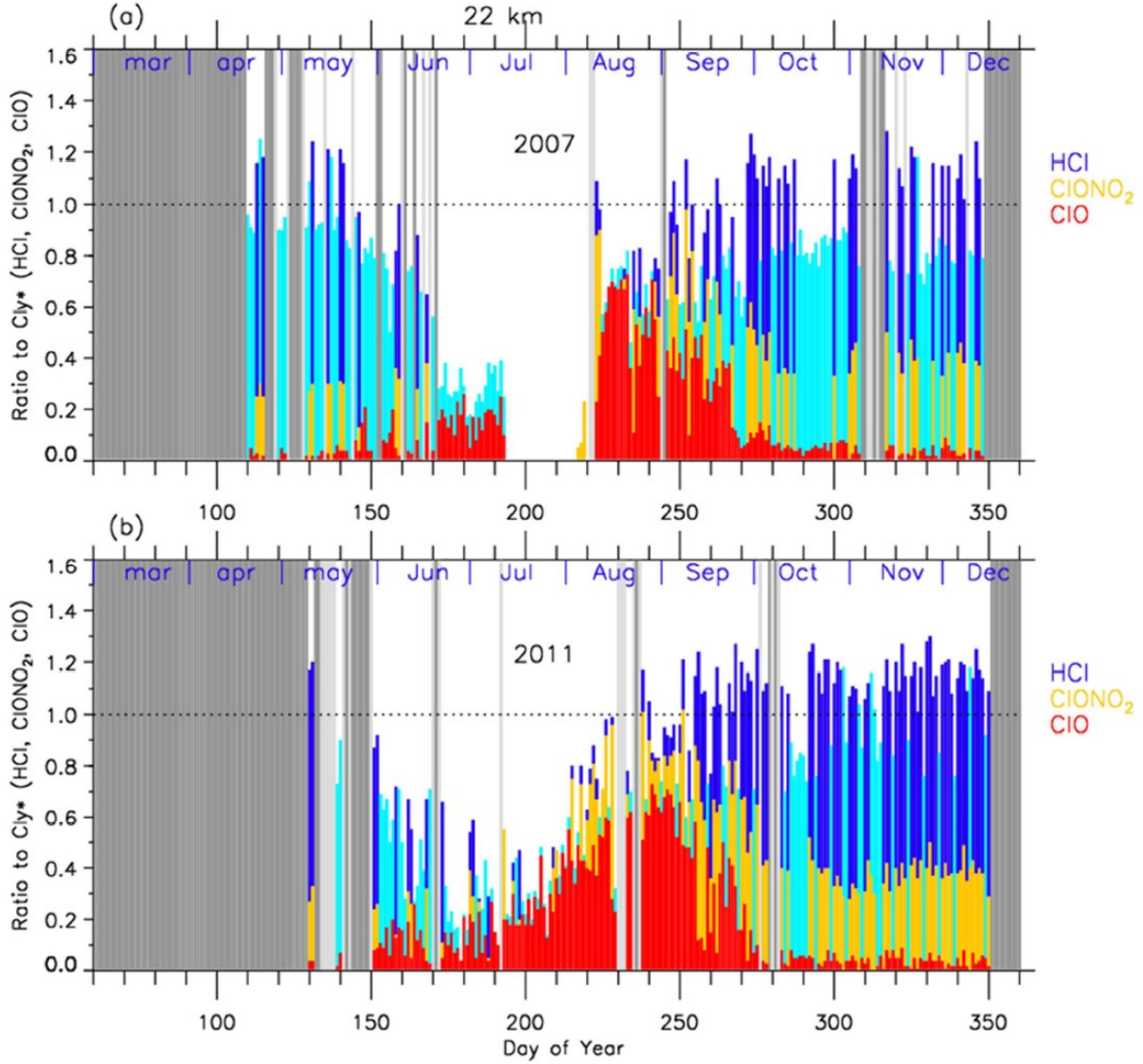


**Figure 9.** Same as Fig. 8 but at 22 km.

<Difference in 22 km compared with 18 km>

- After early September, ClO amount started to decrease, due to deactivation.
- Most Cly were converted into $ClONO_2$ first (early September), and finally HCl also increased at this altitude (22 km).
- The final HCl:$ClONO_2$ ratio after spring is ~3:2

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# Anti-correlation between ClO and $ClONO_2$

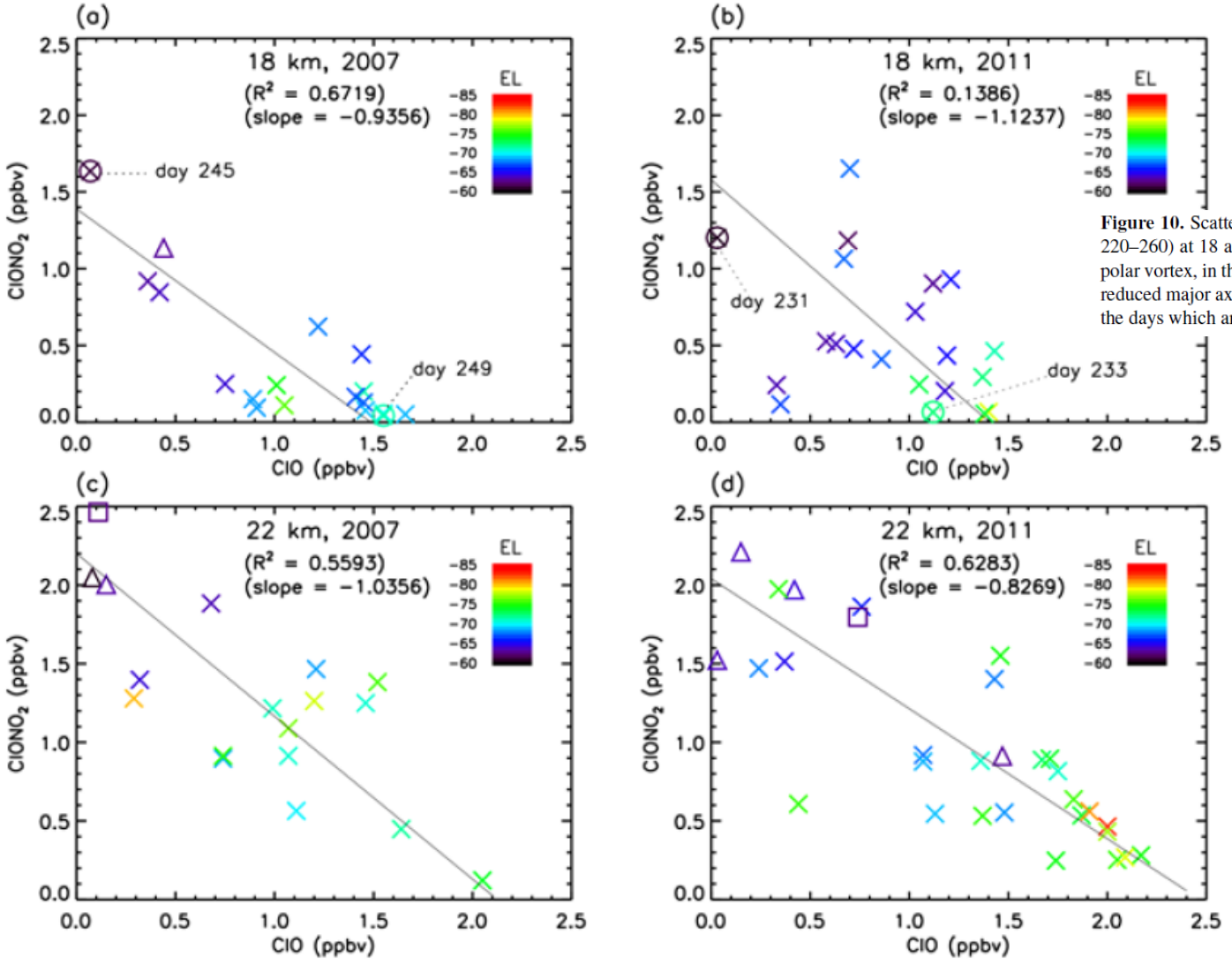


**Figure 10.** Scatter plot between ClO (Aura MLS) and $ClONO_2$ (Envisat MIPAS) mixing ratios between 8 August and 17 September (day 220–260) at 18 and 22 km in 2007 and 2011. Crosses, triangles, and squares represent the data when Syowa Station was located inside the polar vortex, in the boundary region of the polar vortex, and outside the polar vortex, respectively. Solid lines are regression lines obtained by reduced major axis (RMA) regression. Color represents the equivalent latitude over Syowa Station on that day. Circles with crosses represent the days which are shown in Figs. 13 and 14.

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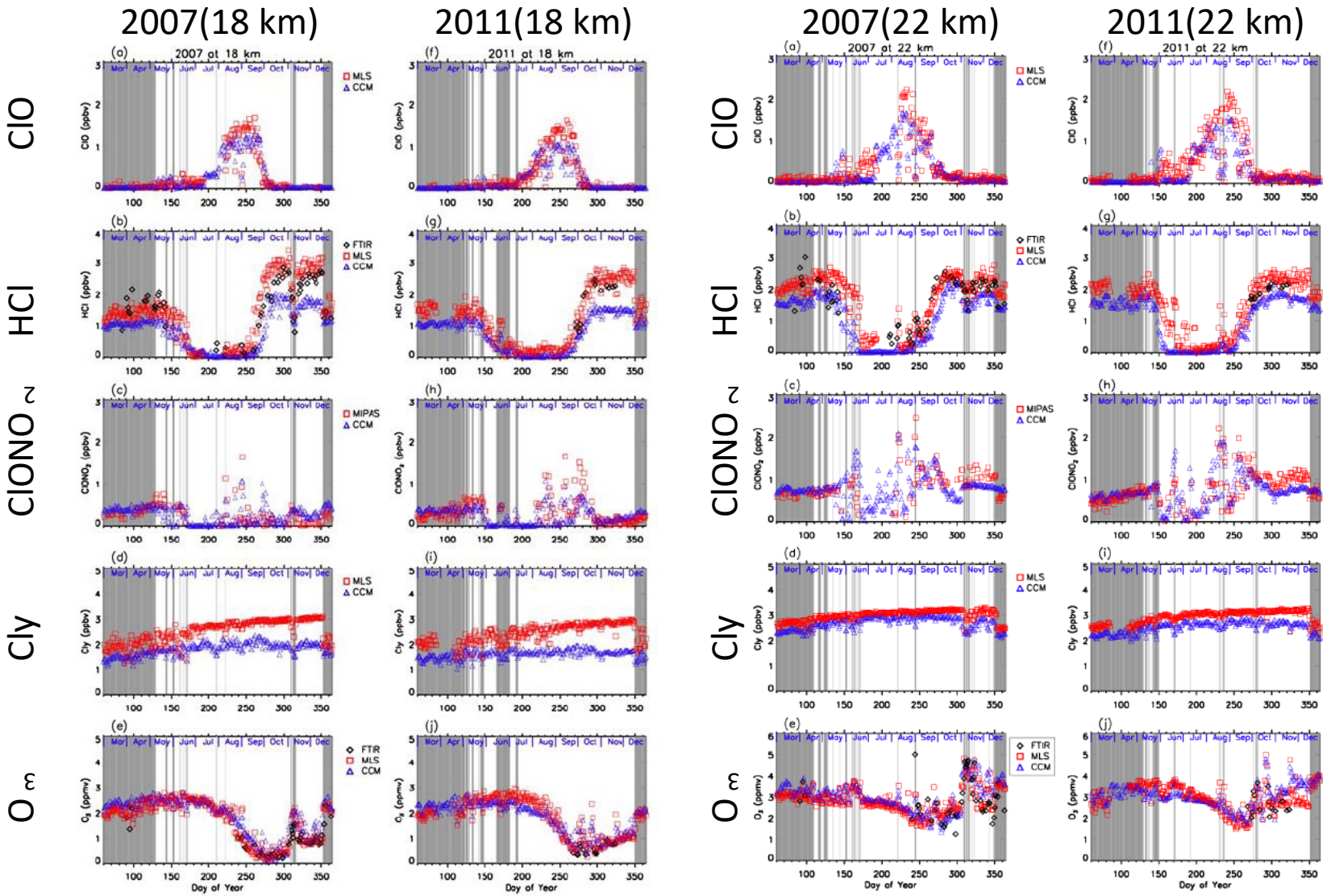
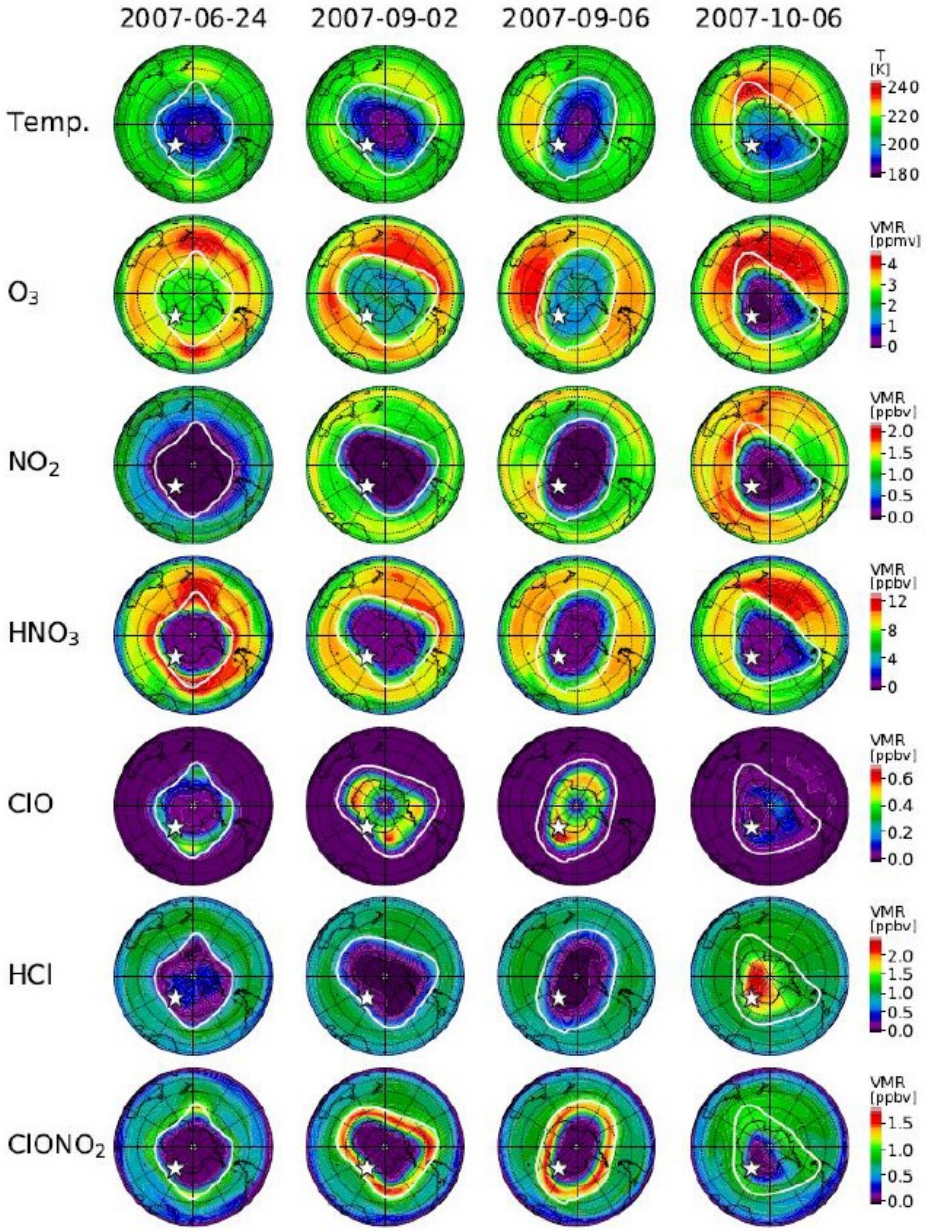
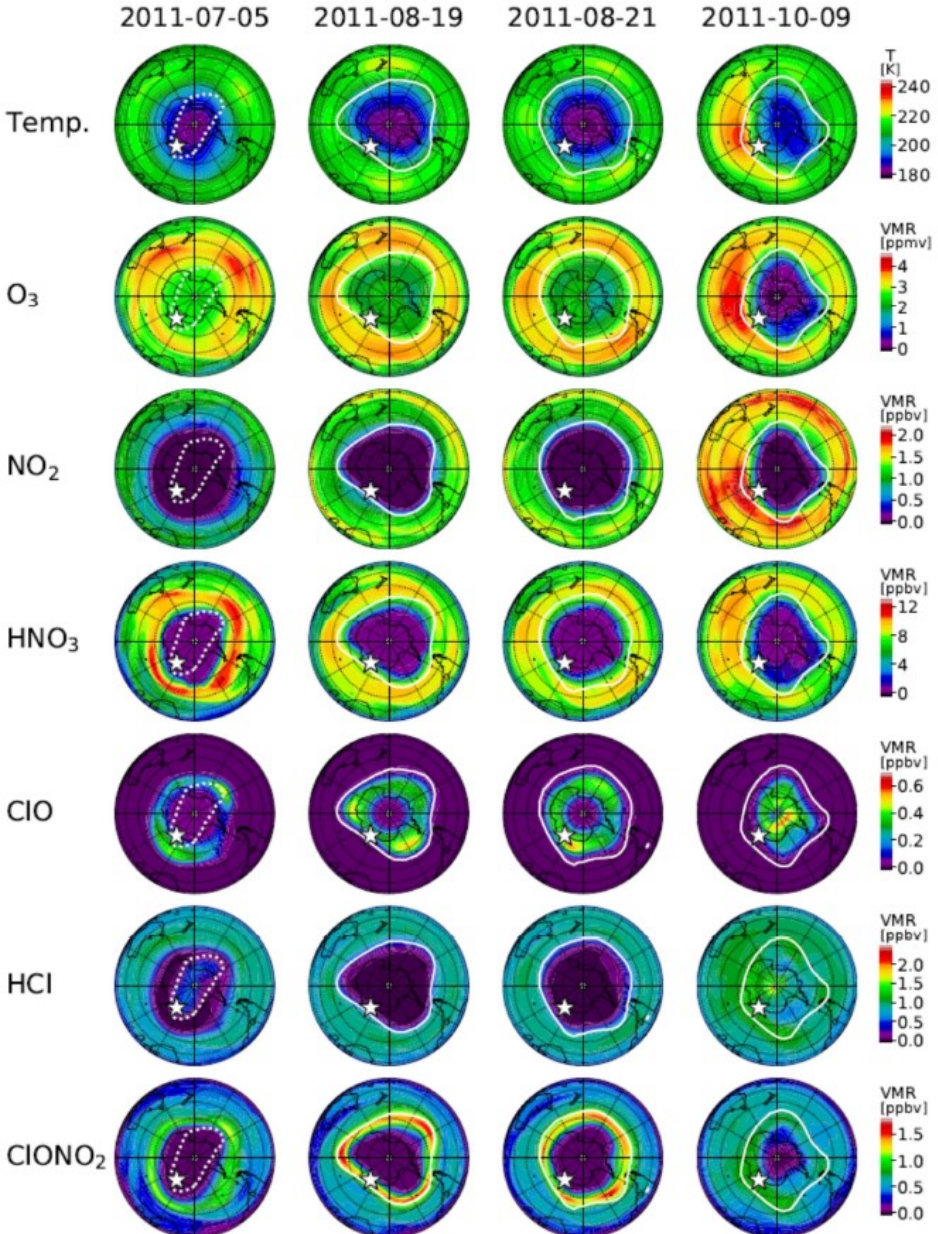
# Comparison between Observations and MIROC3.2 CCM Results

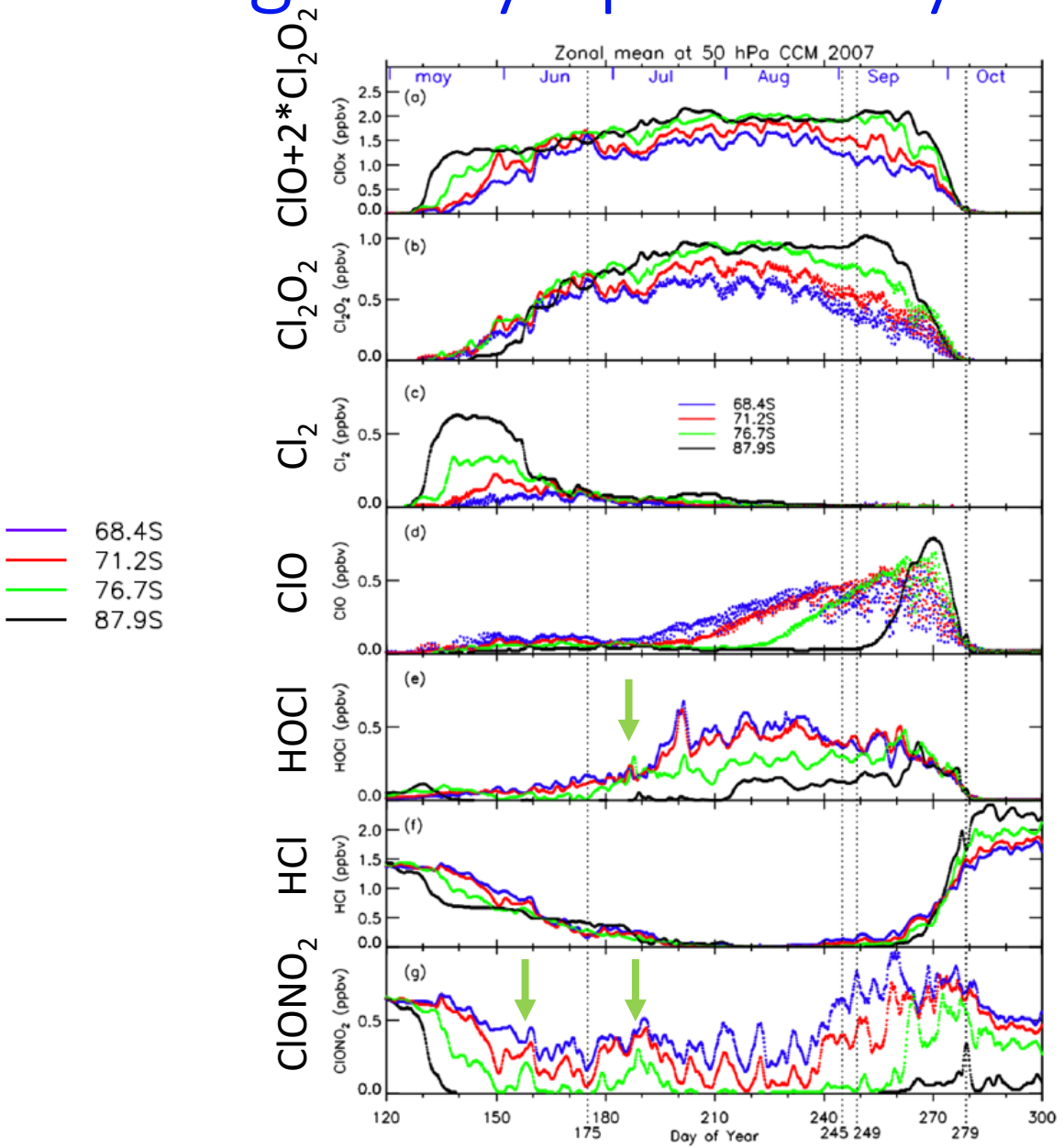


# (2007) MIROC3.2 CCM Results (2011)



# Zonal Averaged Cly Species by MIROC 3.2 CCM




MIROC3.2 CCM

[Akiyoshi et al., JGR, 2016]

T42 (2.8˚x 2.8˚) horizontal,
34 vertical layers,
Top: 80 km (0.01 hPa),
ERA-Interim wind & T,
13 heterogeneous reactions
on PSCs & aerosols,
JPL-2010 coeff.

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# Summary

(1) Chlorine species (HCl, $ClONO_2$, ClO) and $O_3$ was continuously monitored throughout the year over Syowa Station, Antarctica in 2007/2011.

(2) Winter chlorine activation (→ClO) and spring deactivation (→HCl or $ClONO_2$) was detected at 18 and 22 km, in 2007/2011.

(3) Anti-correlation between ClO and $ClONO_2$ during the ClO enhanced period was due to the relative distance of Syowa Station to the polar vortex edge.

(4) Continuous loss of HCl during winter after $ClONO_2$ extinction is thought to be due to transport of outer-vortex $NO_x$ rich air to inside the vortex.

(5) Selective recovery of reservoir species HCl and $ClONO_2$ was revealed in each altitude, depending on $O_3$ and $NO_x$ amount in September/October.