HCl/Cly ratios just before the breakup of the Antarctic vortex as observed by SMILES/MLS/ACE-FTS

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ABSTRACT

The International Space Station/Japanese Exposure Module (ISS/JEM) borne instrument, the Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES), has successfully measured chemical species in the middle atmosphere between October 2009 and April 2010. We focus on inorganic chlorine species measured inside the late spring Antarctic vortex, when hydrogen chloride (HCl) was a main component of the total inorganic chlorine (Cly). Comparisons with other satellite instruments, the Aura Microwave Limb Sounder (MLS) and Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS), are also presented to show the SMILES HCl and chlorine monoxide (ClO) data quality.

Keywords: SMILES, JEM, ISS, MLS, ACE-FTS, HCl, ClO, Cly, polar vortex

1. INTRODUCTION

To observe the time evolution of hydrogen chloride (HCl) in the Antarctic vortex (lower stratosphere) is of importance since HCl acts as a reservoir for the chlorine radicals (ClOx) that destroy ozone catalytically. It is also useful to evaluate model studies of the time series of HCl. ClOx is elevated by heterogeneous reactions in winter and consequently through photolysis/photochemical reactions in spring, then it is deactivated into more inert forms. So far, increased amounts of HCl in the springtime Antarctic when ClOx is deactivated were first observed by ground-based Fourier Transform Infrared Spectroscopy (FTIR) instruments starting in 1987.[1–3] The partitioning of total inorganic chlorine (Cly), which is defined as the sum of Cl, chlorine monoxide (ClO), HOCl, ClOOCl, OClO, chlorine nitrate ($ClONO_2$), HCl, etc., has been investigated in the Arctic (e.g., Ref. 4) using *in situ* aircraft instruments; simultaneous measurements of ClO, HCl, and $ClONO_2$ are available since 1997.[5] While in the Antarctic, no comprehensive aircraft campaign has been done since the 1994 mission.[6] Using the satellite instruments in 1990's, several studies showed the time evolution of ClO and HCl in the spring Antarctic vortices (e.g., Refs. 7–11). Although a short period measurement, the shuttle-borne instrument (combined with the above-mentioned aircraft mission) in 1994 suggested that the high HCl/Cly ratio ($\sim$0.9) was maintained in the November Antarctic vortex.[12,13] Also, in November 1996, it was reported that the high HCl and low $ClONO_2$ were, respectively, observed by HALogen Occultation Experiment (HALOE) and Improved Limb Atmospheric Spectrometer (ILAS) satellite instruments.[14] All of these results confirm a theoretical study by Ref. 15 who showed a mechanism for increased HCl values after the 'ozone hole' period in the Antarctic. This can be understood as low values of ozone shifting the partitioning of ClOx (= Cl + ClO + ClOOCl) into Cl,

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so that the reaction $Cl + CH_4$ that forms HCl proceeds faster than the reaction $ClO + NO_2 + M$ that forms $ClONO_2$, thus reaching a steady state with a high HCl/Cly ratio.

After 2004, this feature has been seen every year in the combined data from the Aura Microwave Limb Sounder (MLS) and the Atmospheric Chemistry Experiment-Fourier transform spectrometer (ACE-FTS) data[16,17] or just in the MLS data.[18,19] Considering the observations and model results so far, a characteristic of the elevated value of HCl/Cly ratio is only seen in this time period (after October) and area (inside the Antarctic vortex) in the lower stratosphere (i.e., other than the upper stratosphere). This results from the combination of diabatic descent of air inside the vortex, low ozone values, and isolation of the lower stratospheric vortex through at least November.

The International Space Station (ISS) borne instrument, the Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES), started operations in October 2009 (see next section in detail). In November 2009, there were some temporary measurements in the Antarctic ($\leq$ 66°S) due to a docking of a shuttle, although SMILES normally observes latitudes between 65°N and 38°S. The breakup of the Antarctic vortex in the lower stratosphere occurred in December 2009,[20] so that some measurements were taken inside the vortex. In this report, we focus on this November, and analyze the vertical profiles of HCl and ClO in the lower stratosphere to confirm those data quality from a view point of the chlorine partitioning. Furthermore, comparisons with other satellite data in the same time are also made and the quantitative results are summarized.

2. MEASUREMENTS OF SMILES

SMILES is a passive sensor to measure the limb of Earth's atmosphere in the frequency bands around 625 and 650 GHz. The instrument was attached to the Japanese Experiment Module (JEM) onboard ISS. The emission lines of O_3, HCl, ClO, HO_2, HOCl, BrO, and other molecules can be found in the low-noise spectra obtained with the 4-K mechanical cooler and superconductor-insulator-superconductor (SIS) mixers. The SMILES observations started on October 12, 2009 and ceased on April 21, 2010 due to the failure of a critical component in the submillimeter local oscillator. Results from SMILES have demonstrated its high potential for observing atmospheric minor constituents in the middle atmosphere, as shown in Ref. 21

The JEM/SMILES mission is a joint project of the Japan Aerospace Exploration Agency (JAXA) and the National Institute of Information and Communications Technology (NICT). The SMILES Level 2 (L2) data processing systems[22,23] retrieve vertical profiles of the atmospheric minor constituents from the calibrated radiance observations (Level 1 data). The SMILES version 2.1 L2 operational products[24] (hereafter L2-v2.1) and the version 2.1.5 L2 research products (hereafter L2r-v2.1.5) were publicly released on March 5, 2012 (`http://smiles.tksc.jaxa.jp/` and `http://smiles.nict.go.jp/`). We used these products in the following section.

Since SMILES has three specified detection bands: 624.32-625.52 GHz (Band A), 625.12-626.32 GHz (Band B), and 649.12-650.32 GHz (Band C) with two acousto-optical spectrometers, observations of Bands A, B, and C are made on a time-sharing basis, such as Bands A+B, A+C, or B+C. In the period that we analyze, the Bands B+C measurements were performed. The $H^{35}Cl$ rotational transition ($J = 1$–0) is located at 625.9 GHz in Band B. The ClO transitions in the ground ro-vibronic state ($J = 35/2$–$33/2$) are located at 649.445 and 649.451 GHz in Band C. Vertical resolution is 3.5-4.1 km. For previous versions of L2 operational products, precision is less than 10% both for HCl at 20-60 km and for ClO at 25-45 km.[21,25,26] For ClO of L2r-v2.1.5, precision is estimated to be 100 and 30 pptv between 100 and 10 hPa.[27] For HCl from the L2 research product, precision is 10%.[23] Detailed validation studies for both of the L2-v2.1 and L2r-v2.1.5 products are, to date, in preparation.

3. METHOD

In November 2009, the Antarctic vortex exhibited a typical seasonal march: it developed in June, maximized around September, and then diminished in the late November/December period.[20] We analyzed the SMILES data obtained on November 19-24, when the measurements were conducted between 38°N and 66°S. In those days, the polar vortex was somewhat shifted toward the South America, so that the edge of the vortex reached to around 50°S in the lower stratosphere.[28] Therefore, we extracted the SMILES data between 50 and 66°S. To categorize observed data from a view point of potential vorticity (PV), we used equivalent latitude (EqL, the

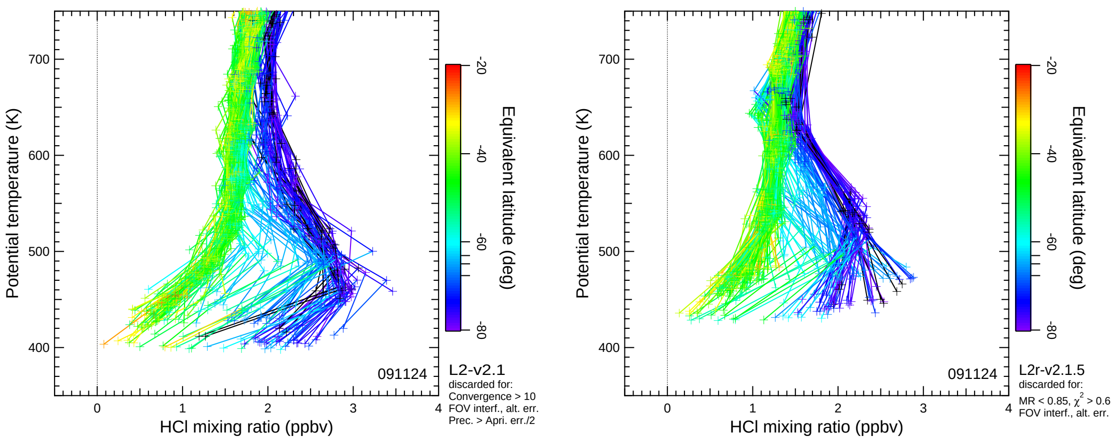

Figure 1. Vertical profiles, as a function of potential temperature, of HCl mixing ratios as measured by SMILES on November 24, 2009: (a) left panel; L2 product of version 2.1 and (b) right panel; L2 research product of version 2.1.5. Data are taken at latitudes between 50 and 66° and color-scaled by equivalent latitudes (EqL). Profiles with EqL less than –80° are shown as black. The outer, center, and inner edges of the vortex at 460 K level are assigned as three small ticks in the EqL color-scale, for reference. Note that the mixing ratio of $H^{35}Cl$ is shown in (b), see text.

latitude that would enclose the same area between it and the pole as a given PV contour[29]) at each measurement location, as mentioned below. In order to show the quality of the SMILES data for studying Cly partitioning inside the Antarctic vortex, we attempt to make comparisons with other satellite data.

In the same period as above, the MLS instrument on the National Aeronautics and Space Administration's (NASA) Earth Observing System (EOS) Aura satellite[30] has operated between 82°N and 82°S. MLS measures millimeter- and submillimeter-wavelength thermal emission from the limb of Earth's atmosphere. We used data products of HCl and ClO retrieved with the version 3.3 data processing algorithm[31] (`http://mls.jpl.nasa.gov/`). The quality of the HCl data is as follows:[32] vertical resolution in the lower stratosphere is ∼3 km and precision is 0.3-0.2 ppbv at 100-10 hPa. The quality of the ClO data is as follows:[32] vertical resolution is 3-4.5 km, precision is ±0.3 ppbv at 147 hPa and ±0.1 ppbv at 100-22 hPa, and bias estimates are from –0.1 to zero ppbv at 50-70°S in November. In this study, we used data taken at 50-66°S. Data screening is also done according to Ref. 32.

ACE-FTS, the primary instrument on the SCISAT-1 satellite, is a high-resolution infrared Fourier transform spectrometer that measures solar occultation spectra between 2.2 and 13.3 μm.[33] It has also operated in the period of November 19-24 at latitudes between 65.7 and 69.3°S from the satellite sunrise measurements. Vertical resolution is 3-4 km. We used data products of HCl and $ClONO_2$ retrieved with the version 3 data processing algorithm[34] (`http://www.ace.uwaterloo.ca/`). The error analysis of the HCl data has not yet been evaluated, but the measurement variability that provides an upper limit on retrieval precision is estimated to be on the order of 5% at 20-55 km.[35] The fitting error of the $ClONO_2$ data is below 10% at 20-30 km and increases to 40% at 14 km.[36]

For both the MLS and ACE-FTS measurement locations and times, Derived Meteorological Products (DMPs) are produced to facilitate comparisons between different satellite instruments.[37] They include potential temperature (PT), PV, EqL, horizontal winds and tropopause locations. In this study, we used DMPs derived from the NASA Global Modeling and Assimilation Office's (GMAO) Goddard Earth Observing System (GEOS) data set (version 5).[38] Using DMPs to view measurements with respect to their air mass characteristics is valuable in a study of chemistry and dynamics inside/outside the vortex. To compare SMILES measurements with those from MLS and ACE-FTS, we also obtained DMPs for the SMILES measurements for the study period.

4. RESULTS AND DISCUSSION

Figure 1 shows vertical profiles of SMILES HCl taken on November 24, 2009 at latitudes between 50 and 66°S as a function of PT. PTs of 400, 500, 600, and 700 K approximately correspond to altitudes of 15, 19, 23,

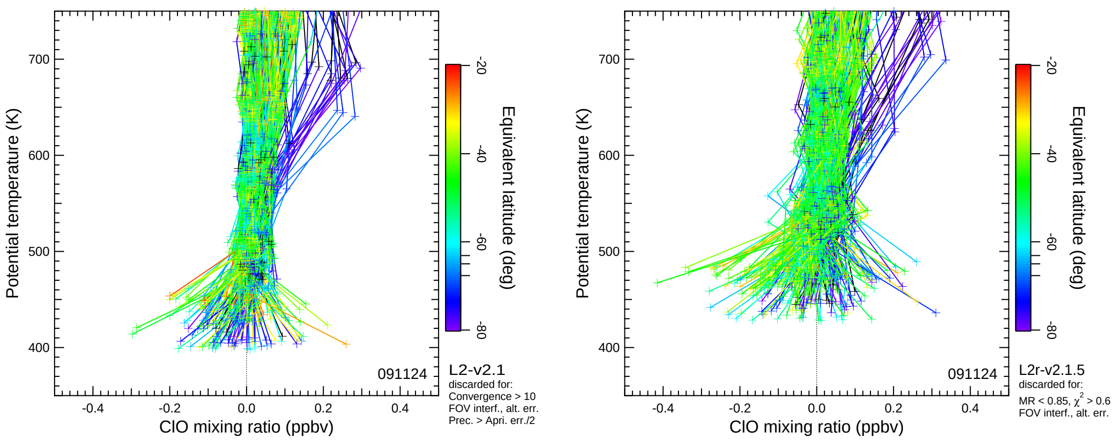

Figure 2. Same as Fig. 1, but for ClO mixing ratios as measured by SMILES.

and 26 km, respectively. For mixing ratios of L2r-v2.1.5 HCl, those of $H^{35}Cl$ are shown (the abundance ratio between $H^{35}Cl$ and $H^{37}Cl$ is 0.757587:0.242257). Each profile is color-scaled by EqL (only apparent in online version). The vortex center is located at $\sim -65°$EqL (negative values are assigned in the southern hemisphere), so that data points with bluish colors mean observations that made inside the vortex. It is thus obvious that profiles taken inside or outside the Antarctic vortex are separately distributed in respect to the HCl mixing ratios below ∼600 K level: high values are found inside the vortex up to 3 ppbv. It should be noted that the profiles are discarded for flag with 'field-of-view interference' and 'altitude error' according to a release note (`http://smiles.isas.jaxa.jp/access/indexe.shtml`). Profiles with 'convergence' value grater than 10 and 'chi-square' value larger than 0.6 are discarded for L2-v2.1 and L2r-v2.1.5, respectively. Further, data points with precision larger than a half of *a priori* error and measurement response smaller than 0.85 are also discarded for L2-v2.1 and L2r-v2.1.5, respectively.

Since Cly in the stratosphere in 2009 was ∼3.3-3.5 ppbv,[39] it is clear that HCl dominates Cly in this altitude range and time period. Such a feature is usually not seen in the lower stratosphere. This feature is explained as a result of low O_3 values ('ozone hole') in October, as follows (e.g., Ref. 11). The two competing reactions of the NO radical:

$$NO + ClO \rightarrow Cl + NO_2 \tag{1}$$

$$NO + O_3 \rightarrow O_2 + NO_2 \tag{2}$$

are the key to understanding this behavior. Under the 'ozone hole' condition with low O_3 and high ClO values, reaction (1) becomes faster than reaction (2), allowing increased value of Cl. The low O_3 value directory slows the reaction:

$$Cl + O_3 \rightarrow ClO + O_2 \,. \tag{3}$$

Thus, the production of HCl occurs rapidly through the reaction:

$$Cl + CH_4 \rightarrow HCl + CH_3 \,. \tag{4}$$

HCl is destroyed through reactions with the OH radical and on the surface of sulfate aerosols, but both are so slow that the chemical lifetime of HCl is long enough compared to transport time in November. The results shown here from the SMILES measurements confirm past measurements in 1990's[7–14] and recent measurements,[16–19] suggesting a high HCl/Cly ratio in this area and time period even in 2009.

As for ClO, SMILES measured low values (less than 0.1 ppbv) below 600 K level, as shown in Figure 2. Because the local time of observation varies, a diurnal change in ClO value exists: the profiles inside the vortex with solar zenith angles (SZA) less than 85° show increased values of up to 0.3 ppbv at 700 K level. Observations with SZA larger than 95° reveal ClO values around zero (not shown). These results also confirm that ClO was spent to reform HCl through the reactions (1) and (4).

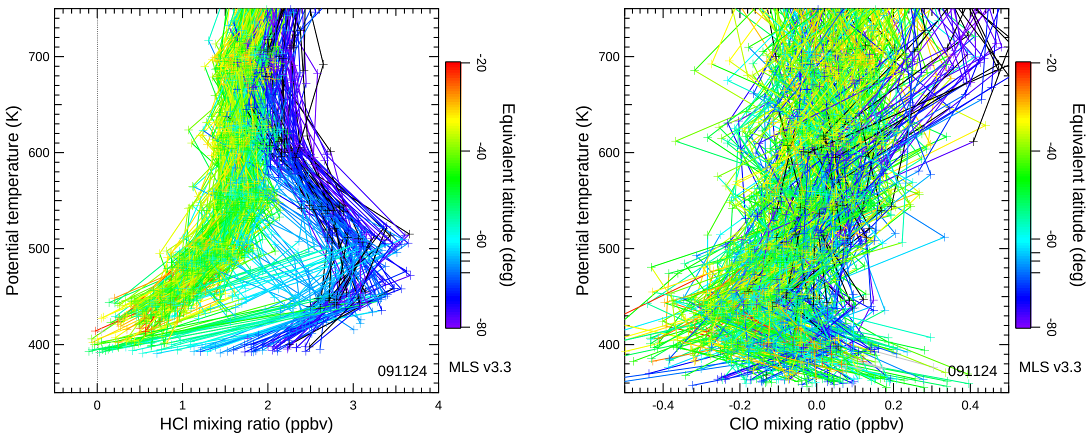

Figure 3. Vertical profiles of mixing ratios of HCl, (a) left panel, and ClO, (b) right panel, as measured by MLS on November 24, 2009 as a function of potential temperature. L2 product of version 3.3 is used. Data are taken at latitudes between 50 and 66° and color-scaled by equivalent latitudes (EqL). Profiles with EqL less than –80° are shown as black. The outer, center, and inner edges of the vortex at 460 K level are assigned as three small ticks in the EqL color-scale, for reference.

Figure 3 shows vertical profiles of HCl, (a), and ClO, (b), taken by MLS on November 24, 2009 at latitudes between 50 and 66°S as a function of PT. Similar to the results of SMILES, the HCl values increased to ∼3.5 ppbv inside the vortex around 500 K level. The absolute value is 10-20% larger than that of SMILES (less than ∼3 ppbv) at the maximum mixing ratios. In this period, Band 13 (primary to detect $H^{35}Cl$) of the MLS instrument was not used and HCl was retrieved using Band 14; it has been suggested that retrievals of HCl from Band 14 have a high bias at high HCl values (above ∼3 ppbv).[32] With this in mind, HCl measurements by SMILES and MLS agrees with each other considering the range of precision.

ClO mixing ratios from MLS also show less than 0.3 ppbv below 600 K level (Fig. 3(b)). Similar to the results of SMILES, the ClO values increased to 0.4-0.5 ppbv above 600 K level inside the vortex. Most of those data are taken at SZAs less than 85°. Like HCl, the absolute value is 0.1-0.2 ppbv larger than that of SMILES. Mixing ratio fluctuations above 500 K are smaller in SMILES than in MLS, reflecting the difference in system noise temperatures between the two instruments.[21] It should be noted that some negative biases in the MLS data are found below 500 K level, amounting to –0.1 ppbv. This is close to a result reported by Ref. 32.

Figure 4 shows vertical profiles of HCl, (a), and $ClONO_2$, (b), taken by ACE-FTS on November 19-24, 2009 at latitudes between 65.7 and 69.3°S as a function of PT. Since the ACE-FTS measurements are made using the solar occultation, observations are limited to a certain latitude in a certain period. However, there are, by chance, observations in those latitudes on the same days as SMILES, although the latitudes are somewhat more southerly than those of SMILES. Similar to the results of SMILES and MLS, the HCl values increased to ∼3 ppbv inside the vortex around 500 K level. The absolute value agrees with SMILES within ±10% below 500 K level. It is of importance to examine chlorine species other than HCl and ClO. Because of the reactions (1) through (4), the formation of $ClONO_2$ by ClO + NO_2 + M is suppressed significantly inside the vortex, revealing the mixing ratios less than 0.2 ppbv below the 500 K level. Above the 500 K level, it increases with altitude to 1.2 ppbv around 700 K level.

Finally, we examine the partitioning of Cly inside the vortex. We take Cly values as the sum of HCl, ClO during the daytime (SZA less than 85°), and $ClONO_2$. For ACE-FTS, ClO of SMILES L2-v2.1 is added, instead of the ACE-FTS ClO, to the sum of HCl and $ClONO_2$ values. Figure 5 shows vertical profiles of each chlorine species inside the vortex (within the vortex center) between 19 and 24 November, 2009. Data are binned by a 25 K PT interval between 400 and 700 K. The average and one sigma standard deviation are shown for ClO and HCl values (only the average is shown for $ClONO_2$). The ratios between HCl and Cly are shown in the right panel. Good agreement among the three sensors is evident for all PT levels. As we discussed so far, the HCl/Cly

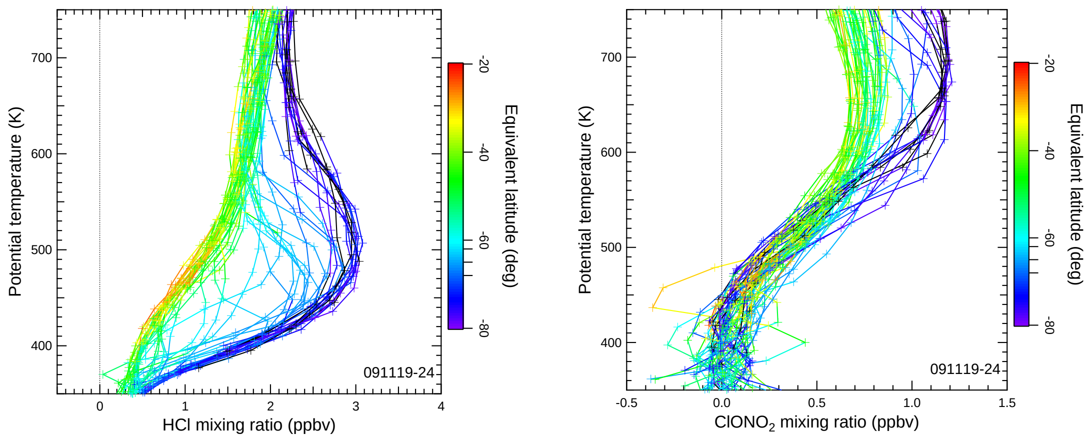

Figure 4. Vertical profiles of mixing ratios of HCl, (a) left panel, and $ClONO_2$, (b) right panel, as measured by ACE-FTS on November 19-24, 2009 as a function of potential temperature. L2 product of version 3 is used. Data are taken at latitudes between 65.7 and 69.3° and color-scaled by equivalent latitudes (EqL). Profiles with EqL less than –80° are shown as black. The outer, center, and inner edges of the vortex at 460 K level, on average for 6 days, are assigned as three small ticks in the EqL color-scale, for reference.

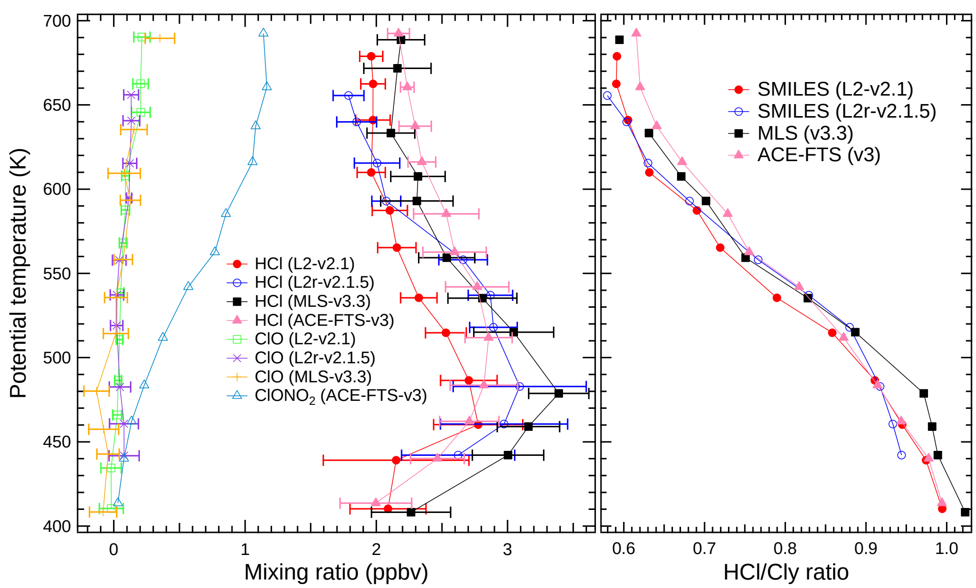

Figure 5. Vertical profiles of each chlorine species, (a) left panel, and HCl/Cly ratio, (b) right panel, as measured by SMILES, MLS, and ACE-FTS on November 19-24, 2009 inside the Antarctic vortex as a function of potential temperature. For a derivation of Cly, see text.

ratio is greater than 0.9 below 500 K level. This strongly suggests that even in the late November period HCl dominates Cly inside the Antarctic vortex in the lower stratosphere.

5. CONCLUDING REMARKS

SMILES has measured several chemical species in the middle atmosphere between October 2009 and April 2010. It is onboard the ISS/JEM platform and measures successfully the low-noise emission spectra with the 4-K mechanical cooler and SIS mixers. We focus on inorganic chlorine species measured inside the late spring Antarctic vortex on November 19-24, 2009. The data are sorted by PT/EqL with the aid of DMPs. The results shows that HCl is a main component of Cly below 500 K level. In this period, other satellite instruments, MLS and ACE-FTS, have also operated. Both of MLS and ACE-FTS also show high HCl values inside the vortex. All of the three sensors show high values ($\sim$0.9) of the HCl/Cly ratios inside the vortex. The results presented here suggest the validity of the SMILES HCl and ClO data in the lower stratosphere both for L2-v2.1 and L2r-v2.1.5 data products. Further updates to both of the retrieval algorithm are ongoing and will be available to open public (the second release), including the updated quality of some minor species (e.g., HOCl).

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