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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We retrieved lower stratospheric vertical profiles of O_3, HNO_3, and HCl from solar spectra taken with a ground-based Fourier-Transform infrared spectrometer (FTIR) installed at Syowa Station, Antarctica (69.0˚ S, 39.6˚E) from March to December 2007 and September to November 2011. This was the first continuous measurements of chlorine species throughout the ozone hole period from the ground in Antarctica. We analyzed temporal variation of these species combined with ClO, HCl, and HNO_3 data taken with the Aura/MLS (Microwave Limb Sounder) satellite sensor, and $ClONO_2$ data taken with the Envisat/MIPAS (The Michelson Interferometer for Passive Atmospheric Sounding) satellite sensor at 18 and 22 km over Syowa Station. HCl and $ClONO_2$ decrease occurred from the end of May at both 18 and 22 km, and eventually in early winter, both HCl and $ClONO_2$ were almost depleted. When the sun returned to Antarctica in spring, enhancement of ClO and gradual O_3 destruction were observed. During the ClO enhanced period, negative correlation between ClO and $ClONO_2$ was observed in the time-series of the data at Syowa Station. This negative correlation was associated with the relative distance between Syowa Station and the edge of the polar vortex. We used MIROC3.2 Chemistry-Climate Model (CCM) results to investigate the behavior of whole chlorine and related species inside the polar vortex and the boundary region in more detail. From CCM model results, rapid conversion of chlorine reservoir species (HCl and $ClONO_2$) into Cl_2, gradual conversion of Cl_2 into Cl_2O_2, increase of HOCl in winter period, increase of ClO when sunlight became available, and conversion of ClO into HCl, was successfully reproduced. HCl decrease in the winter polar vortex core continued to occur due to both transport of $ClONO_2$ from the subpolar region to higher latitudes, providing a flux of $ClONO_2$ from more sunlit latitudes into the polar vortex, and the heterogeneous reaction of HCl with HOCl. Temporal variation of chlorine species over Syowa Station was affected by both heterogeneous chemistries related to Polar Stratospheric Cloud (PSC) occurrence inside the polar vortex, and transport of a NOx-rich airmass from the polar vortex boundary region which can produce additional $ClONO_2$ by reaction of ClO with NO_2. The deactivation pathways from active chlorine into reservoir species (HCl and/or $ClONO_2$) were confirmed to be highly dependent on the availability of ambient O_3. At 18 km where most ozone was depleted, most ClO was converted to HCl. At 22km where some O_3 was available, additional increase of $ClONO_2$ from pre-winter value occurred, similar as in the Arctic.

Keywords: chlorine species, ozone, Antarctica, Syowa Station, FTIR, satellite