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# Partitioning between the inorganic chlorine reservoirs HCl and $ClONO_2$ during the Arctic winter 2005 from the ACE-FTS

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## Abstract

From January to March 2005, the Atmospheric Chemistry Experiment high resolution Fourier transform spectrometer (ACE-FTS) on SCISAT-1 measured many of the changes occurring in the Arctic (50–80° N) lower stratosphere under very cold winter conditions. Here we focus on the partitioning between the inorganic chlorine reservoirs HCl and $ClONO_2$ and their activation into ClO. The simultaneous measurement of these species by the ACE-FTS provides the data needed to follow chlorine activation during the Arctic winter and the recovery of the Cl-reservoir species $ClONO_2$ and HCl. The time evolution of HCl, $ClONO_2$ and ClO as well as the partitioning between the two reservoir molecules agrees well with previous observations and with our current understanding of chlorine activation during Arctic winter. The results of a chemical box model are also compared with the ACE-FTS measurements and are generally consistent with the measurements.


## 1. Introduction

The key role of chlorine species in the depletion of ozone occurring during cold Arctic winters and under high chlorine loading is now well demonstrated (WMO, 2002). A schematic description of the winter conversion of chlorine reservoir molecules to photochemically active species and of the subsequent reformation of the reservoir species in the spring is given by Michelsen et al. (1999, Plate 8). When the temperatures are sufficiently low to allow the formation of polar stratospheric clouds (PSCs), the chlorine reservoir species HCl and $ClONO_2$ are transformed by heterogeneous reactions into active chlorine molecules ($ClO_x$=ClO+2$Cl_2O_2$+2$Cl_2$) that drive catalytic ozone destruction. In the Arctic, the peak of the ClO volume mixing ratio profile is about 20–21 km and the chlorine activation typically extends up to ~25 km (Santee et al., 2003). In the presence of gaseous nitric acid (which allows the formation of $NO_x$ from the photolysis of $HNO_3$ and also from the reaction with OH) and modest levels of ozone (which allows



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the formation of ClO via Cl+$O_3$), typical of the Arctic, $ClO_x$ deactivation proceeds by the formation of $ClONO_2$ by the three body reaction of ClO and $NO_2$. The reformation of HCl via the reaction of Cl and $CH_4$ is slower than the formation of $ClONO_2$. The strong denitrification, or at least the lack of gaseous $HNO_3$, and the lack of $O_3$ in the Antarctic prevents the rapid recovery of $ClONO_2$. The buildup of HCl thus occurs later in the Arctic spring by the slow conversion of $ClONO_2$ into HCl (Douglass et al., 1995; Müller et al., 1994; Santee et al., 1996; Chipperfield at al., 1996).

The time evolution of inorganic chlorine species during the polar winter and the early spring and their partitioning have been studied in both hemispheres from ground-based (Solomon et al., 2000; Mellqvist et al., 2002), airborne (Webster et al., 1993), balloon-borne (Payan et al., 1998; Stachnik et al., 1999), shuttle-borne (Rinsland et al., 1995; Michelsen et al., 1996), and space-borne (Dessler et al., 1995, Douglass et al., 1995; Santee et al., 1996; Höpfner et al., 2004) instruments. However, very few of these instruments (Payan et al., 1998; Stimpfle et al., 1999; Bonne et al., 2000) are able to measure HCl and $ClONO_2$ simultaneously and none have been able to follow their evolution through the winter and spring. As far as we know, the ACE-FTS instrument is the first space-borne instrument capable of measuring HCl, $ClONO_2$, and ClO simultaneously. We report on the time series of the two reservoir molecules during the Arctic winter 2004/2005 and their partitioning as well as the evolution of chlorine monoxide. We compare the results to previous observations and to the calculations from a chemical box model.

## 2. ACE-FTS measurements

The Atmospheric Chemistry Experiment (ACE), also known as SCISAT-1, was launched on 12 August 2003, into a circular, 74° inclination low-earth orbit at 650 km. It has a global coverage from approximately 85° N to 85° S with a majority of measurements over the Arctic and the Antarctic (Bernath et al., 2005). ACE makes solar occultation measurements and can observe up to 15 sunsets and 15 sunrises per day. The



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primary ACE instrument is a high resolution (0.02 $cm^{-1}$) Fourier transform spectrometer (ACE-FTS) operating between 750 and 4400 $cm^{-1}$. Vertical profiles of temperature, pressure and various atmospheric constituents are retrieved, with a vertical resolution of 3–4 km, from the ACE-FTS spectra recorded at a series of tangent heights, using a global fit approach coupled with a Levenberg-Marquardt non-linear least squares method (Boone et al., 2005). The results presented herein correspond to version 2.2 of the retrieval algorithm using the HITRAN2004 linelist (Rothman et al., 2005). Molecular absorption lines are fitted in selected microwindows to determine temperature and volume mixing ratio profiles. A set of microwindows is determined for each target species and is optimized to reduce the impact of interferers and to retrieve the vertical profile over the broadest possible altitude range. HCl is retrieved between 8 and 57 km from a set of 22 microwindows with a maximum width of 0.5 $cm^{-1}$ in the 2700–3000 $cm^{-1}$ spectral range. The main interferers are $CH_4$ and $O_3$ and they are retrieved simultaneously with the target species. McHugh et al. (2005) showed in an initial comparison using version 1.0 (using only 13 microwindows for HCl and a reduced altitude range) that ACE HCl abundances are 10 to 20% larger than those of HALOE. More recently, Froidevaux et al. (2005) have found that the MLS HCl values are within ~5% of the ACE values (version 2.1, near-real-time version of version 2.2) in the stratosphere. For $ClONO_2$, two microwindows are used (779.85–780.45 $cm^{-1}$ and 1291.8–1293.4 $cm^{-1}$) to retrieve the profile between 12 and 35 km. The main interferers, $O_3$, $HNO_3$, $N_2O$, and $CH_4$ are also fitted simultaneously, including 3 additional microwindows (1104.78–1105.08 $cm^{-1}$, 1202.61–1203.11 $cm^{-1}$, and 1728.03–1728.53 $cm^{-1}$) to constrain better the interferers. Only a very preliminary validation of ACE-FTS version 1.0 $ClONO_2$ has been made using ground-based FTS instruments (Mahieu et al., 2005). For the few cases of close co-incidence, the agreement between ACE-FTS and ground-based $ClONO_2$ columns is within a few percent. Finally, ClO retrieval is carried out between 11 and 30 km using the spectral window: 821 to 846 $cm^{-1}$. This window is similar to the one used by Glatthor et al. (2004) to retrieve ClO from MIPAS spectra.



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## 3. Synoptic view of the winter 2005 during the observation period

To describe the temperature conditions in the Arctic polar stratosphere we have used the National Centers for Environmental Protection/National Center for Atmospheric Research Reanalysis data (hereinafter "NCEP data") (Kistler et al., 2001). The region of interest for processing $Cl_y$ is largely from 70 hPa and 30 hPa. However, the lowest temperatures are found at 50 hPa (not shown) so we have described the evolution at this pressure level.

In mid-January, on the 50 hPa surface there is a cold pool with temperatures less than 191 K over northern Canada, poleward of 75° N which shifts eastward over Scandinavia and intensifies towards the end of the month. On 25 January the temperature minimum is less than 186 K at 77° N and 8° E. By early February the lowest temperatures, less than 189 K, are over Greenland and located at about 75° N. By 20 February the cold pool is found over the north Atlantic with the temperature minimum under 187 K. A strong warming occurs by the end of February and lasts into March so that temperatures conducive to polar stratospheric cloud formation are no longer present.

For most of January and February a significant region of the Arctic stratosphere has temperatures below 192 K and it is likely that nitric acid trihydrate (NAT) and supercooled ternary solution (STS) PSCs developed (e.g. Kleinböhl et al., 2005; Jin et al, personal communication, 2005, have also seen denitrification using the ACE data). Given the observed water vapor mixing ratios, it is likely that ice and STS PSCs form during late January and late February when temperatures fall below 187 K.

Any bias in the NCEP assimilated temperature data is likely to be towards higher values (Manney et al., 2003) so it is probable that temperatures even less than 186 K were present in early 2005. The spatial extent of the regions with temperatures low enough for PSC formation is sufficient for a significant portion of the vortex confined air mass to experience heterogeneous chemical processing during its slow descent through the 50 hPa surface (e.g. Kleinböhl et al., 2005). It is likely that heterogeneous processing occurred in a larger volume of vortex air than indicated by the NCEP data.

## 4. Results and discussion

For this study we focus on measurements obtained over the Arctic (from 50° N to 80° N) between 1 January 2005 and 26 March 2005. The upper panels of Fig. 1 show the latitudes sounded during the observation time period and the corresponding equivalent latitudes (the latitude that would enclose the same area between it and the pole as a given potential vorticity (PV) contour) at 20.5 km. Each occultation was classified as inside, on the edge or outside the vortex, depending on the position of its reference latitude and longitude relative to the vortex edge. The classification method used here is a slightly modified version of the method described by Nassar et al. (2005). The occultations were classified based on the 15–25 km altitude range that includes the altitude of the maximum of the chlorine activation and of the recovery near 20 km. The edge classification includes both occultations that truly cross the edge of the vortex, as well as those with a mixture of vortex and extravortex characteristics between 15 and 25 km due to the highly variable vortex of the 2005 Arctic winter. The results obtained were also verified by visual inspection of PV maps at 490 K (~18–19 km) from GEOS-4 (Goddard Earth Observing System, Version 4.03) analyses (Bloom et al., 2005).

The three lowest panels of Fig. 1 show the time series of the volume mixing ratios (vmrs) of HCl and $ClONO_2$ and their ratio at 20.5 km from 1 January 2005 to 26 March 2005 for the occultations inside, on the edge and outside the vortex. For occultations defined as extravortex, the HCl vmr values at 20.5 km are about 1.5 ppbv while the $ClONO_2$ vmr values are about 0.75 ppbv, with a $ClONO_2$/HCl ratio of about 0.5 (lowest panel). This ratio value is characteristic of unprocessed air masses and consistent with previous observations (Rinsland et al., 1995) although somewhat lower than that given by the box model (see below). In the case of occultations on the vortex edge, the trends of HCl, $ClONO_2$ and their ratio during the polar winter are more difficult to establish due to the smaller number of measurements near the vortex edge and the greater uncertainty in classification of measurements there. However, their behavior is generally quite similar to the behavior of occultations inside the vortex and the recovery



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of $ClONO_2$ seems to occur first on the edge as described by Chipperfield et al. (1997). In the case of vortex occultations, the large number of measurements permits us to follow all stages from chlorine activation to reservoir molecule recovery. However, it is worth noting that the sampling of air masses within the vortex is poor at the beginning of the observation period (Fig. 1, second panel) but increases during the winter and becomes rather good during the late winter and the early spring (reservoir recovery period). We also note that the occultations measured during most of February correspond to an observation period with very high beta angles (>55° between 7 February and 21 February 2005). The beta angle is the angle between the orbital plane and the earth-sun vector. At high beta angles, the latitudes and longitudes sounded during an occultation vary significantly between the highest and the lowest tangent heights, and the number of measured spectra per occultation increases substantially, which leads to unstable retrievals. Relatively few profiles are available as shown in Fig. 1.

### 4.1. Evolution of HCl inside the vortex

For HCl, the start of the decrease is observed at the beginning of January and becomes more pronounced after 20 January 2005 (Fig. 1). The minimum value of the HCl vmr (~0.2 ppbv) is reached around 25 January and low values persist until 25 February. After this period of very low levels of HCl, a slow recovery occurs from the end of February until the end of our measurement period, when HCl reaches values close to those characteristic of unprocessed air masses.

The correlation plot of HCl versus $CH_4$ between 350 K and 700 K in Fig. 2 shows another view of the evolution of HCl inside the vortex which also allows for descent. Gray circles, corresponding to measurements outside the vortex, are used as a reference for unprocessed air masses. Similar conclusions to those discussed for the level at 20.5 km can be drawn: from the variation it can be seen that HCl is processed progressively and sporadically throughout January. It is also clear from this figure that the HCl is quite variable throughout the vortex. The maximum of HCl processing occurs between 25 January and mid-February and this is followed by a slow recovery of HCl



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during March. We note that HCl is not completely recovered at the end of our measurement period inside air masses remaining from vortex air (the vortex is breaking down during March).

### 4.2. Evolution of $ClONO_2$ inside the vortex

In early January, the $ClONO_2$ vmr in the vortex at 20.5 km is quite variable and the higher values suggest that some processing has already taken place (Fig. 1). From 20 to 30 January the $ClONO_2$ varies from less than 0.1 ppbv to over 1.5 ppbv suggesting that the ACE-FTS is sampling air that has recently undergone processing so there has not been sufficient time to convert the ClO to $ClONO_2$ while the higher values suggest that either the ClO resulting from earlier processing has been converted to $ClONO_2$ (This is also suggested by the ClO plot in Fig. 4 which shows that the ClO has decreased during this period.) or the air masses sampled were not processed (due to the variability in the vortex position with respect to ACE observations).

The $ClONO_2$ variability within the vortex is also clearly shown by the correlation of $ClONO_2$ and $CH_4$ in Fig. 3 for the period 1–25 January (red circles). From 18 February to the beginning of March $ClONO_2$ is also quite variable. The lowest values are not as low as those in January and indicate less extensive processing or mixing of non-vortex air. We note that the $N_2O$-$CH_4$ correlations inside and outside the vortex indicate that there has not been much mixing of non-vortex air during this period (Jin et al, ibid). However, it is worth pointing out that Manney et al. (2006) show evidence of mixing into and within the vortex throughout the winter, and getting stronger in late February. The higher values of $ClONO_2$ (up to 2.2 ppbv), much larger than those typical of unprocessed air masses (gray circles in Fig. 3) suggest that the air parcels have been highly processed and the ClO converted back to $ClONO_2$.

At the 20.5 km level the maximum of $ClONO_2$ vmr occurs between 2 and 10 March, with values between 2 and 2.5 ppbv, consistent with observations made by Payan et al. (1998) during March 1995. After 10 March, $ClONO_2$ decreases as it is slowly converted into HCl. However, as evidenced from the correlation plot (Fig. 3) $ClONO_2$ vmrs



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remain high until 24 March at other levels.

### 4.3. Evolution of the inorganic chlorine partitioning

Concerning the partitioning between HCl and $ClONO_2$, their ratio ($ClONO_2$/HCl) is about 0.5 on average (Fig. 1) during the first stage of chlorine activation (i.e., when both HCl and $ClONO_2$ decrease). When HCl and $ClONO_2$ are both at their lowest levels (25 January–3 February), the ratio increases and varies between 0 and 4 with a significant number of values higher than 1. During this time period, $ClONO_2$ is, in general, higher than HCl because of its re-formation from ClO and $NO_2$ from photolysis of $HNO_3$ as noted above. The recovery begins after 4 February and the $ClONO_2$/HCl ratio reaches values as high as 8 between 18 and 28 February. As HCl begins to recover at the end of February, the ratio decreases progressively until 26 March. The ratio value is between 2.5 and 3 for the first 10 days of March as observed by Payan et al. (1998) during March 1995.

### 4.4. Evolution of ClO inside the vortex

ClO profiles are also retrieved from ACE-FTS spectra. Due to ice contamination on the detector during the measurement period, individual profiles of ClO are not completely reliable and require averaging. We have done this in the following fashion. The occultations were divided into 2 groups in order to average profiles corresponding to similar air masses. Measurements within vortex or on the edge were chosen based on HCl vmrs at 19.5 km and 20.5 km. If these values are lower than 1 ppbv, then the occultations can be averaged together. The reliability of this criterion was checked by averaging ClO profiles corresponding to HCl values higher than 1 ppbv at 19.5 and 20.5 km for periods of 5 days between 1 January and 26 March. The time series obtained is presented in the lower panel of Fig. 4. ClO vmrs are less than 0.4 ppbv and negligible for all altitudes, within one standard deviation.

We average ClO profiles with the following criteria: occultations have to be within 5

days and the difference in latitude should not exceed 2°. Profiles that have unphysical oscillations for the entire altitude range (11–30 km) are also rejected. This is particularly the case for occultations with beta angles higher than 56° (8–19 February). For this special case, only occultations after 15 February have realistic ClO profiles. The criterion based on latitude (2°) is relaxed and the ClO profiles between 15 and 19 February are averaged together. The upper panel of Fig. 4 shows the time series obtained. Sampling is an issue for the reliability of the averages. The average profiles between 20 January and 10 March are based on more than 10 individual profiles and are thus reliable. Outside this time period, the profiles just give the general trend of the time evolution of ClO. Although MLS data show that Cl-activation is significant by the end of December and quite substantial in the first 10 days of January (Santee et al., 2005[1]), the activation is apparent in the ACE data only from 10 January to the beginning of March. Note that polar stratospheric clouds (PSCs) are also observed in some ACE-FTS spectra during this time period (Eremenko et al., 2005[2]). The beginning of chlorine activation corresponds well to the decrease in HCl and $ClONO_2$ levels and the end of activation to the maximum recovery of $ClONO_2$ (2–10 March). Occultations before mid-February correspond to sunrise measurements and occultations after mid-February to sunset measurements. The amounts of ClO are then larger during sunsets than for sunrises when the dimer $Cl_2O_2$ is still present in significant amounts. The maximum vmr value for ClO (about 1.07 ppbv), is reached near 20 km during the period of 15–19 February. This maximum value is smaller than the climatological values derived by Santee et al. (2003, Fig. 2) from MLS/UARS data recorded between 1991 and 1998. These values are between 1.20 and 1.35 ppbv for an equivalent latitude of 74° N (that corresponds to the mean equivalent latitude of ACE-FTS measurements inside the

[1]Santee, M. L., MacKenzie, I. A., Manney, G. L., et al.: A study of stratospheric chlorine partitioning in the winter polar vortices based on new satellite measurements and modeling, in preparation, 2006.

[2]Eremenko, M. N., Galkina, I., Zasetsky, A. Y., and Sloan, J. J.: Case Study of Polar Stratospheric Clouds by ACE-FTS Observations over Scandinavia, in preparation, 2006.

vortex for the time period 15–19 February). It worth noting that only data with a solar zenith angle, SZA<88° (daylight) have been considered by Santee et al. (2003), while ACE-FTS data are given at 90° due to the measurement geometry. The ACE-FTS ClO vmrs are consequently smaller. The maximum ClO value derived from ACE-FTS measurements is also much smaller than values regularly observed in Antarctic (>2 ppbv) (Glatthor et al., 2004; Santee et al., 2003). The mean value of ClO during the activation period is about 0.6–0.7 ppbv corresponding to moderate activation.

## 5. Comparison with a chemical box model

Three-dimensional trajectories were produced using NCEP wind and temperature data. Multiple trajectories were initialized from the January and February ACE occultation locations at different altitudes and evolved for 60 days. Thus although this is not a domain-filling method it should, however, allow a reasonable representation of the type of processing that the ACE measurement locations should have encountered. It should also give a reasonable idea of the variation of species within the vortex, again as viewed by the ACE-FTS instrument. Of course, it is not expected that parcel identity can persist this long in reality, but these trajectories give an indication of the chemical environment present inside the vortex. Some fraction of vortex air will experience multiple heterogeneous chemical processing events while some fraction will not be affected by processing. Mixing will smear out the sharp differences between the air parcels found in the trajectory modelling.

The photochemical calculations have been done with a box model (Chartrand and McConnell, 1998) with updated rate data including heterogeneous chemistry on ice and STS polar stratospheric clouds. The initial chemical concentrations were taken from the ACE-FTS measurement suite; those species which were not observed were taken from the CMAM model (e.g., de Grandpré et al., 2000).

Figure 5 shows one particular trajectory in this suite launched from an ACE measurement location on 9 January, 2005. For this trajectory the HCl is not completely

processed while the $ClONO_2$ virtually disappears. Of the total amount of $Cl_y$, 2.1 ppbv, (and 60% HCl) about 1.9 ppbv is converted to $ClO_x$ (ClO and $Cl_2O_2$). The $ClO_x$ disappears with a time constant of about 2 weeks and the main reservoir species formed is $ClONO_2$: HCl is much slower to reform. By the end of February, the trajectory $ClONO_2$/HCl ratio is about 4.3, somewhat higher than that for the measurements at that period. However this ratio is trajectory (and also temperature) dependent. Other trajectories indicate the gradual processing of vortex air through the cold pool.

Figure 6 presents a composite of $ClONO_2$, HCl and their ratio from the set of vortex trapped trajectories initialized from 22.5, 23.5 and 24.5 km at the time of ACE occultations. For presentation, the values at each time have been averaged and at selected times the variance of the values have been plotted. The detailed trajectories indicate that not all encountered temperatures low enough for significant heterogeneous processing while others encountered extensive processing. This is also evident from the plot in Fig. 6 taking into account the variability in the HCl which shows that HCl varies from very small values indicating rather complete processing to larger values which indicate little processing. This variability is similar to that shown by the measurements in Fig. 1. Where processing does occur the depletion of $ClONO_2$ is generally greater than that for HCl. The processing is clustered around late January and late February when the Arctic cold pool reaches its lowest temperatures as described above. The behavior of $ClONO_2$ and the $ClONO_2$/HCl ratio in Fig. 6 has some resemblance to Fig. 1 in regards to the timing of the depletion and the reformation and increase in chlorine nitrate. An important difference between Figs. 1 and 6 is that while Fig. 1 is for a fixed altitude, Fig. 6 shows concentrations from a range of altitudes between 16 km and 24.5 km, with values at later stages tending to be at lower altitudes. Air sampled on the 50 hPa surface will capture parcels affected by heterogeneous chemistry during the peak processing period but at later stages will see unprocessed parcels from higher altitudes.

The lowest panel in Fig. 6 shows the ClO that results from the processing. Bearing in mind the variability shown the values are comparable with those of the measurements



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shown in Fig. 5. However, we have not reproduced the ClO feature that is measured at about day 15. The box model lacks representation of polar stratospheric cloud types that are not either ice or STS and temperatures below 191 K cover a large region in the first half of January 2005. The significant ClO values observed indicate that NAT processing was present.

## 6. Summary and conclusions

We have presented the first time series from space of the processing and recovery of the primary chlorine reservoirs HCl and $ClONO_2$ in the Arctic polar vortex for the period January to March 2005 using the high resolution ACE-FTS. We also present average measurements for ClO during this period. The time evolution of HCl, $ClONO_2$ and ClO as well as the partitioning between the two reservoir molecules agrees well with previous observations and confirms our current understanding of chlorine activation during Arctic winter (Michelsen et al., 1999). Figure 7 presents a summary of the evolution of HCl, $ClONO_2$ and of their ratio inside the Arctic vortex 2005. In early January the measurements (ClO in particular) indicate processing of the vortex air. The decrease in HCl and $ClONO_2$ begins after 10 January. HCl vmrs stay very low until the end of February and HCl recovers slowly until 26 March. The first recovery of $ClONO_2$ occurs between 9 February and the end of February and reaches a maximum between 2 and 10 March. Moreover, since the ACE-FTS samples a range of vortex latitudes during this period it also samples to what extent the vortex air has been processed. Using a box model and measurements, the picture that emerges is consistent with our understanding of PSC processing. As vortex air is processed through the cold pool and circulates in the vortex, the chlorine reservoirs HCl and $ClONO_2$ are gradually converted to $ClO_x$. The ACE-FTS thus samples air that is freshly processed with low HCl and $ClONO_2$ values and high ClO vmrs as well as air that has been partially processed and air which is beginning to recover pre-processing reservoir vmrs. Further analysis and comparison with measured ozone loss is in progress and should yield further insights to the 2005



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Arctic ozone loss period.

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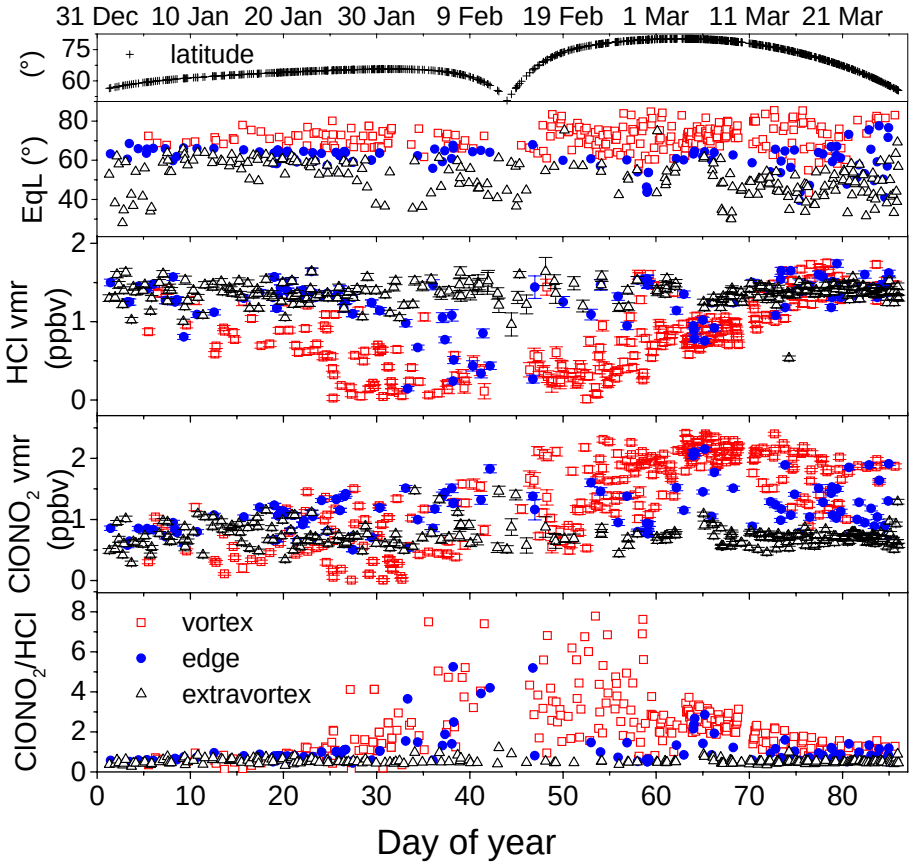


**Fig. 1.** Polar latitudes sounded by ACE-FTS and the corresponding equivalent latitudes (upper panels) and time series of HCl, $ClONO_2$ and their ratio at 20.5 km (lower panels) during the Arctic winter 2005.



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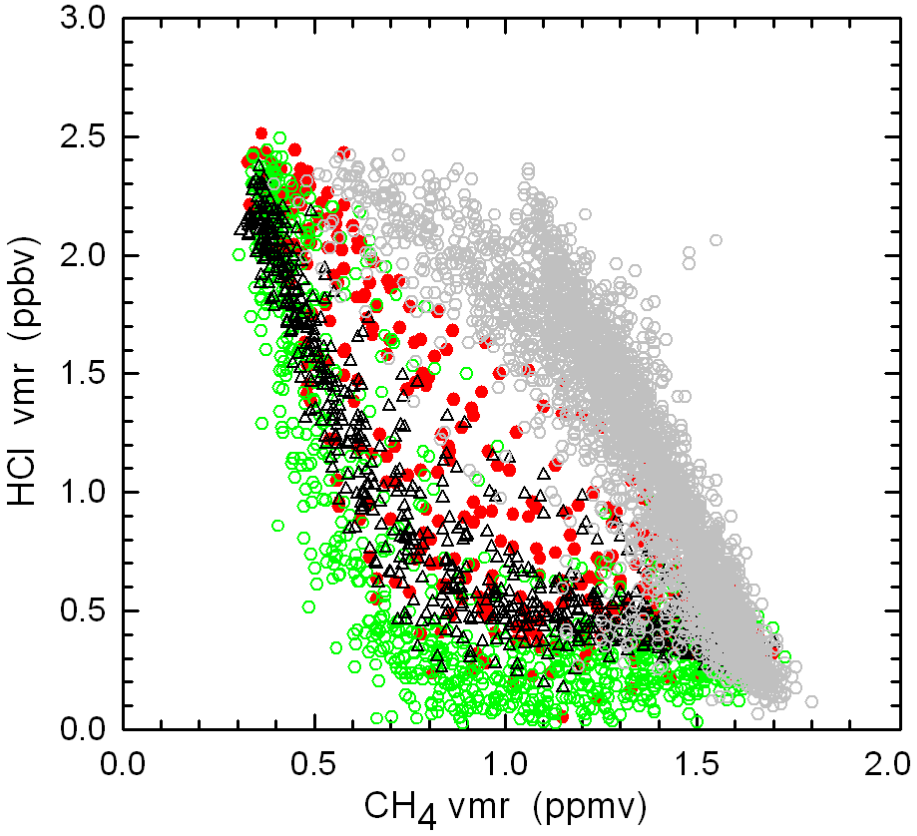


**Fig. 2.** Correlation plot of HCl versus $CH_4$ between 350 K and 700 K. Gray circles are observations outside the vortex at 3 January–26 March 2005; red dots are observations in the vortex at 1–25 January 2005; green circles are observations in the vortex at 26 January–25 February 2005; black triangles are observations in the vortex at 26 February–24 March 2005.



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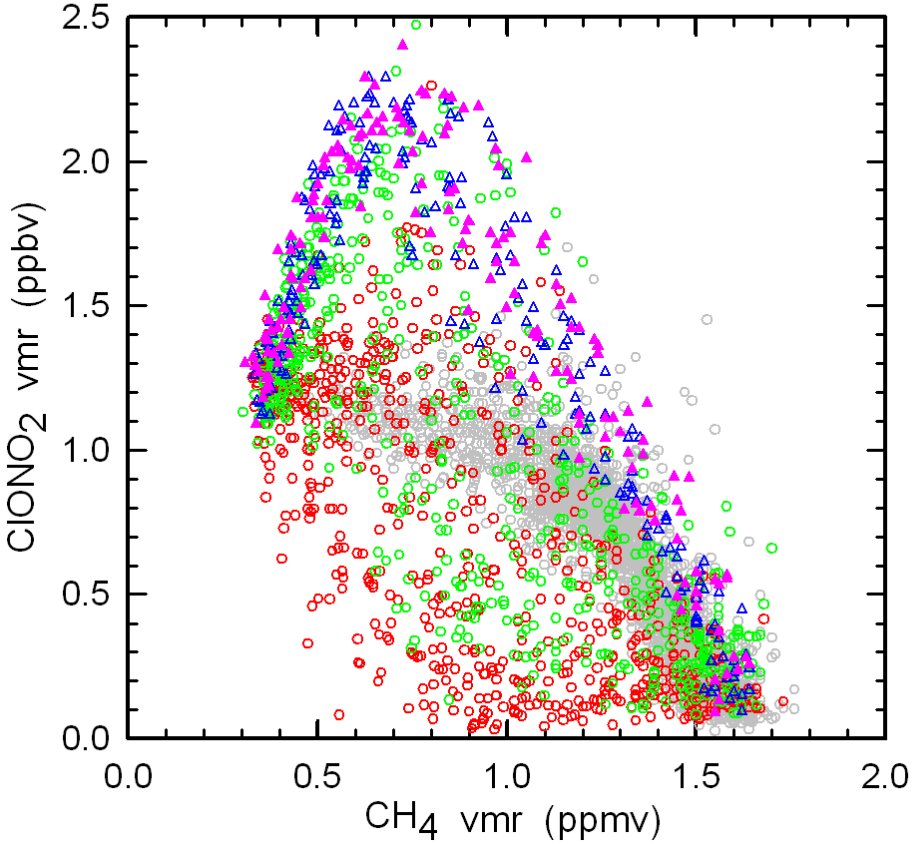


**Fig. 3.** Correlation plot of $ClONO_2$ versus $CH_4$ between 350 K and 700 K. Gray circles are observations outside the vortex at 1 January–26 March 2005; color symbols are observation in the vortex: red circles, 3 January–15 February 2005; green circles, 16–28 February 2005; blue triangles, 2–9 March 2005; purple triangles, 11–24 March 2005.



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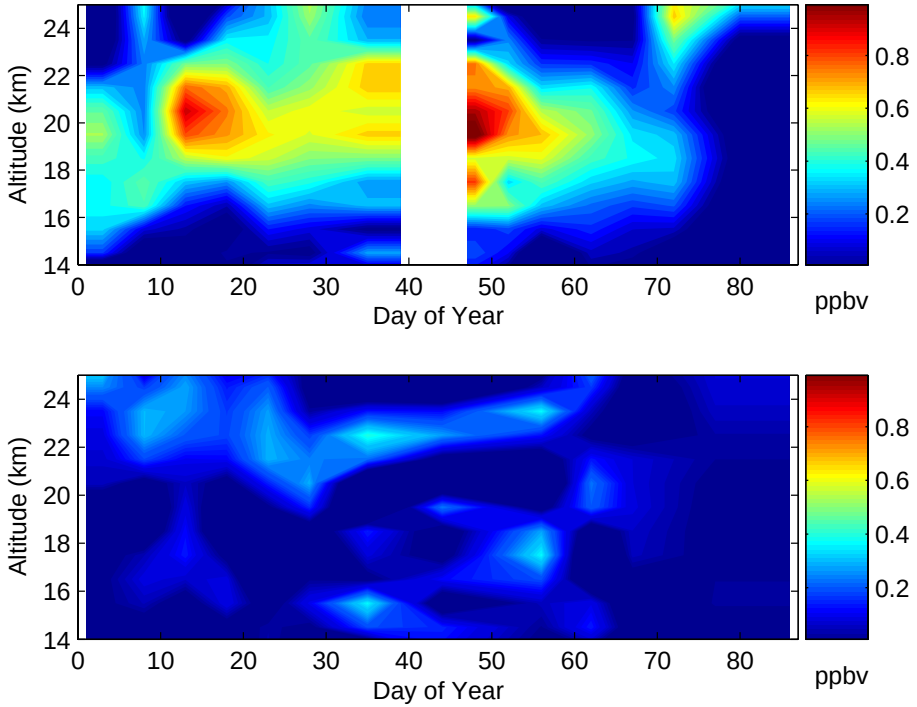


**Fig. 4.** Time series of average ClO profiles between 14 and 25 km during the Arctic winter 2005. Upper panel: measurements corresponding to processed air masses. Lower panel: measurements corresponding to unprocessed air masses (see text for details).



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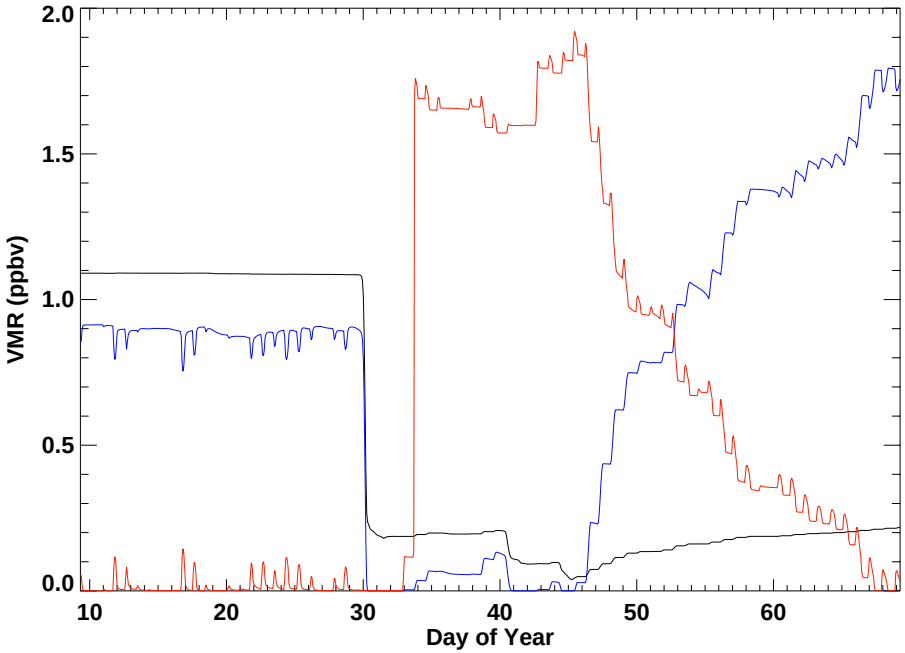


**Fig. 5.** HCl (black), $ClONO_2$ (blue) and ClOx (loosely defined as $ClO+2Cl_2O_2$) (red) vmrs for a 3-D trajectory launched from an ACE observation location (61.1° N, 49.8° E) at 06:00 GMT on 9 January 2005 and followed out for 60 days, using NCEP data. For initial conditions see text.



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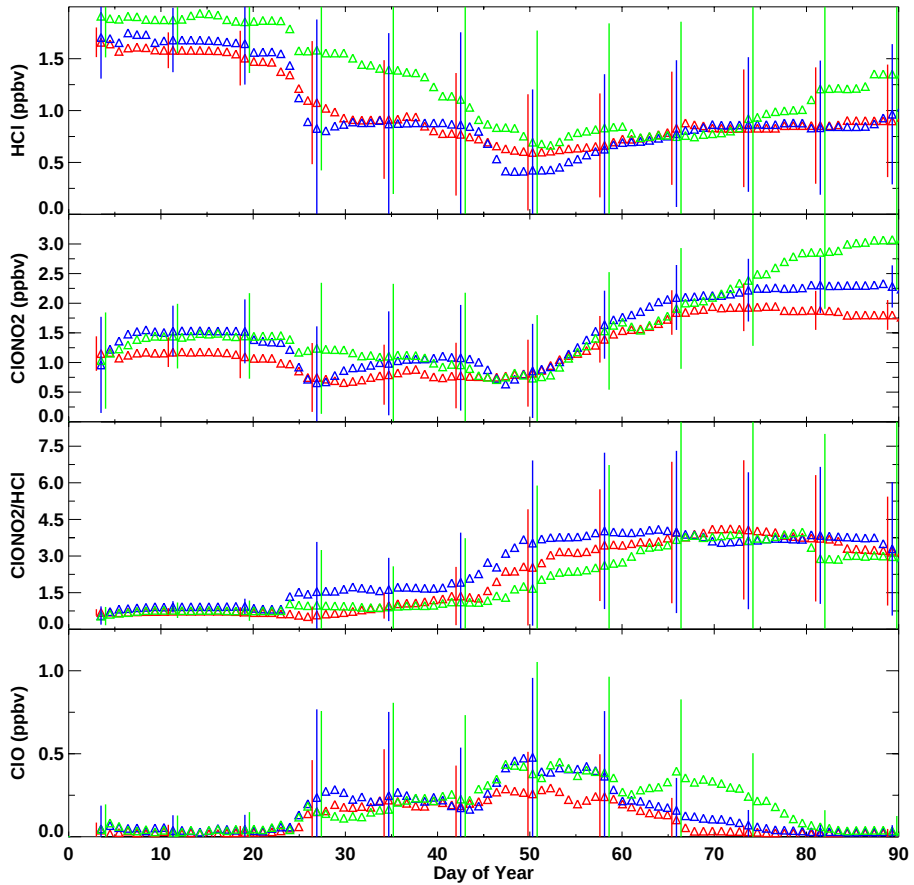


**Fig. 6.** Mean concentrations versus day of year for HCl (first panel), $ClONO_2$ (second panel), $HCl/ClONO_2$ ratio (third panel) and ClO (fourth panel) from vortex trapped trajectories. Colours represent different altitudes from which trajectories were initialized: 22.5 km (red), 23.5 km (blue) and 24.5 km (green). Error bars based on variance are shown at select times.



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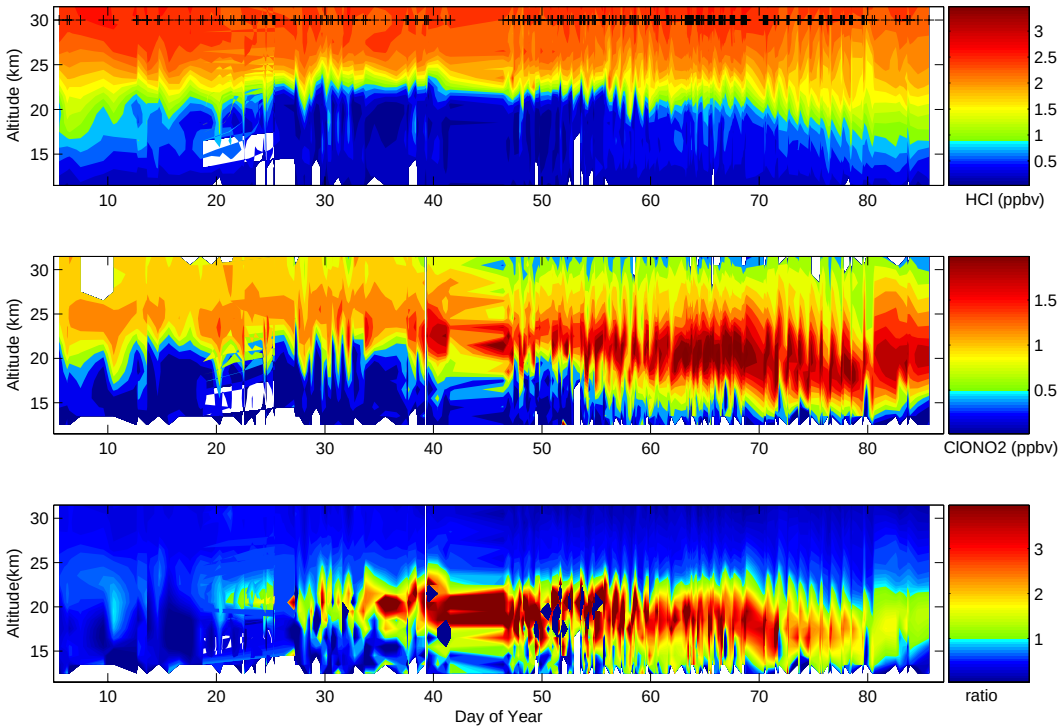


**Fig. 7.** Time series of the HCl (top), $ClONO_2$ (middle) and $ClONO_2$/HCl (bottom) profiles between 10 and 31 km observed from 1 January 2005 to 26 March 2005 for measurements inside the vortex. Crosses on the top panel represent the actual measurement time. White areas correspond to missing data.



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