

# HOCl chemistry in the Antarctic Stratospheric Vortex 2002, as observed with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS)

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**Abstract.** In the 2002 Antarctic polar vortex enhanced HOCl mixing ratios were detected by the Michelson Interferometer for Passive Atmospheric Sounding both at altitudes of around 35 km (1000 K potential temperature), where HOCl abundances are ruled by gas phase chemistry and at around 18–24 km (475–625 K), which belongs to the altitude domain where heterogeneous chlorine chemistry is relevant. At altitudes of 33 to 40 km polar vortex HOCl mixing ratios were found to be around 0.14 ppbv as long as the polar vortex was intact, centered at the pole, and thus received relatively little sunlight. This is the altitude region where in midlatitudinal and tropic atmospheres peak HOCl mixing ratios significantly above 0.2 ppbv (in terms of daily mean values) are observed. After deformation and displacement of the polar vortex in the course of a major warming, ClO-rich vortex air was more exposed to sunlight, where enhanced HO<sub>x</sub> abundances led to largely increased HOCl mixing ratios (up to 0.3 ppbv), exceeding typical midlatitudinal and tropical amounts significantly. The HOCl increase was preceded by an increase of ClO. Model runs could reproduce these measurements only when the Stimpfle et al. (1979) rate constant for the reaction ClO+HO<sub>2</sub>→HOCl+O<sub>2</sub> was used but not with the current JPL recommendation. At an altitude of 24 km, HOCl mixing ratios of up to 0.15 ppbv were detected. This HOCl enhancement, which is already visible in 18 September data, is attributed to heterogeneous chemistry, which is in agreement with observations of polar stratospheric clouds. The measurements were compared to a model run where no polar stratospheric clouds appeared during the observation period. The fact that HOCl still was produced in the model run sug-

gests that a significant part of HOCl was generated from ClO rather than directly via heterogeneous reaction. Excess ClO, lower ClONO<sub>2</sub> and earlier loss of HOCl in the measurements are attributed to ongoing heterogeneous chemistry which is not reproduced by the model. On 11 October, polar vortex mean daytime mixing ratios were only 0.03 ppbv.

## 1 Introduction

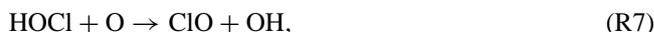
The HOCl catalytic cycle (Solomon et al., 1986) is an important mechanism for mid-latitude stratospheric ozone loss (Lary, 1997):



Other HOCl removal reactions are



and

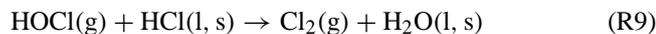


which is more efficient at higher altitudes if enough atomic oxygen is available. Further, in winter polar stratospheric vortices HOCl is generated by heterogeneous chemistry:



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and further converted to  $\text{Cl}_2$ , a precursor of ozone depleting  $\text{ClO}_x$  radicals, via the heterogeneous reaction

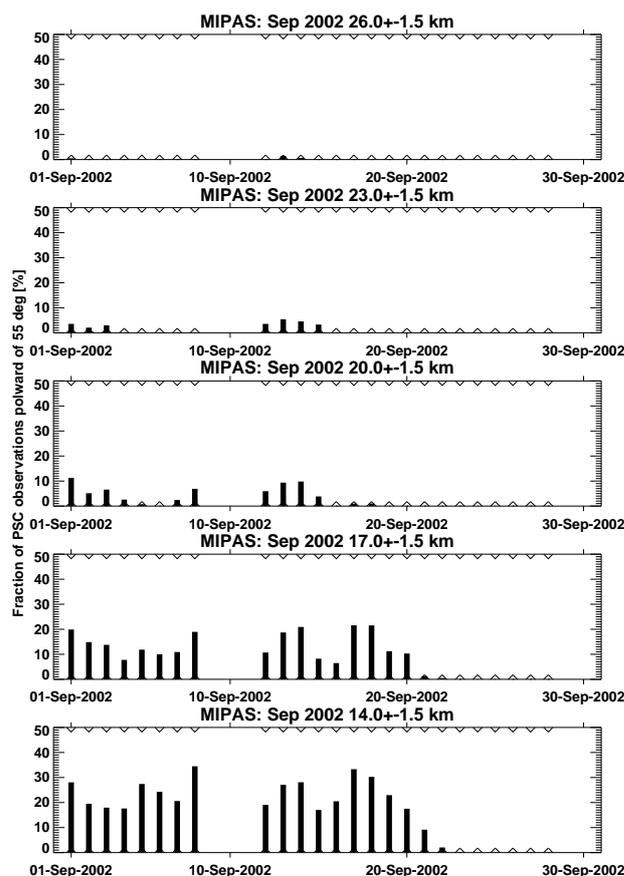


(Hanson and Ravishankara, 1992; Abbatt and Molina, 1992; Crutzen et al., 1992; Prather, 1992), where (g), (l), and (s) indicate gaseous, liquid or solid phase, respectively, for typical polar stratospheric conditions.

However, there do not exist many experimental data which can be used to study polar stratospheric HOCl chemistry quantitatively. Midlatitudinal HOCl measurements are available from balloon- and airborne infrared solar absorption measurements (Larsen et al., 1985; Toon et al., 1992), spaceborne infrared solar occultation measurements (Raper et al., 1987), and balloon-borne far infrared limb emission measurements (Chance et al., 1989; Traub et al., 1990; Johnson et al., 1995). Arctic stratospheric balloon-borne infrared limb emission measurements were analyzed for HOCl by von Clarmann et al. (1997). Kovalenko et al. (2007) have found that the rate constant for Reaction (R1) as suggested by Stimpfle et al. (1979) is more consistent with both infrared solar occultation and far infrared emission measurements of HOCl than the current JPL recommendation (Sander et al., 2006). The first global HOCl distribution was measured with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) (von Clarmann et al., 2006). These data give evidence of enhanced abundances in the Antarctic polar vortex at an altitude of approximately 18–24 km (475–625 K). This enhancement was attributed to heterogeneous chemistry, since polar stratospheric clouds had been observed in advance of these measurements (Höpfner et al., 2004) (see also Fig. 1). In this paper, the temporal development of Antarctic stratospheric HOCl abundances is analyzed in more detail and put into the context of MIPAS ClO (Glatthor et al., 2004) and ClONO<sub>2</sub> (Höpfner et al., 2004) measurements. In order to better understand the temporal development of the measured abundances of chlorine species, these are compared to those calculated with the Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA; Kouker et al. 1999; Ruhnke et al. 1999a; Reddmann et al. 2001).

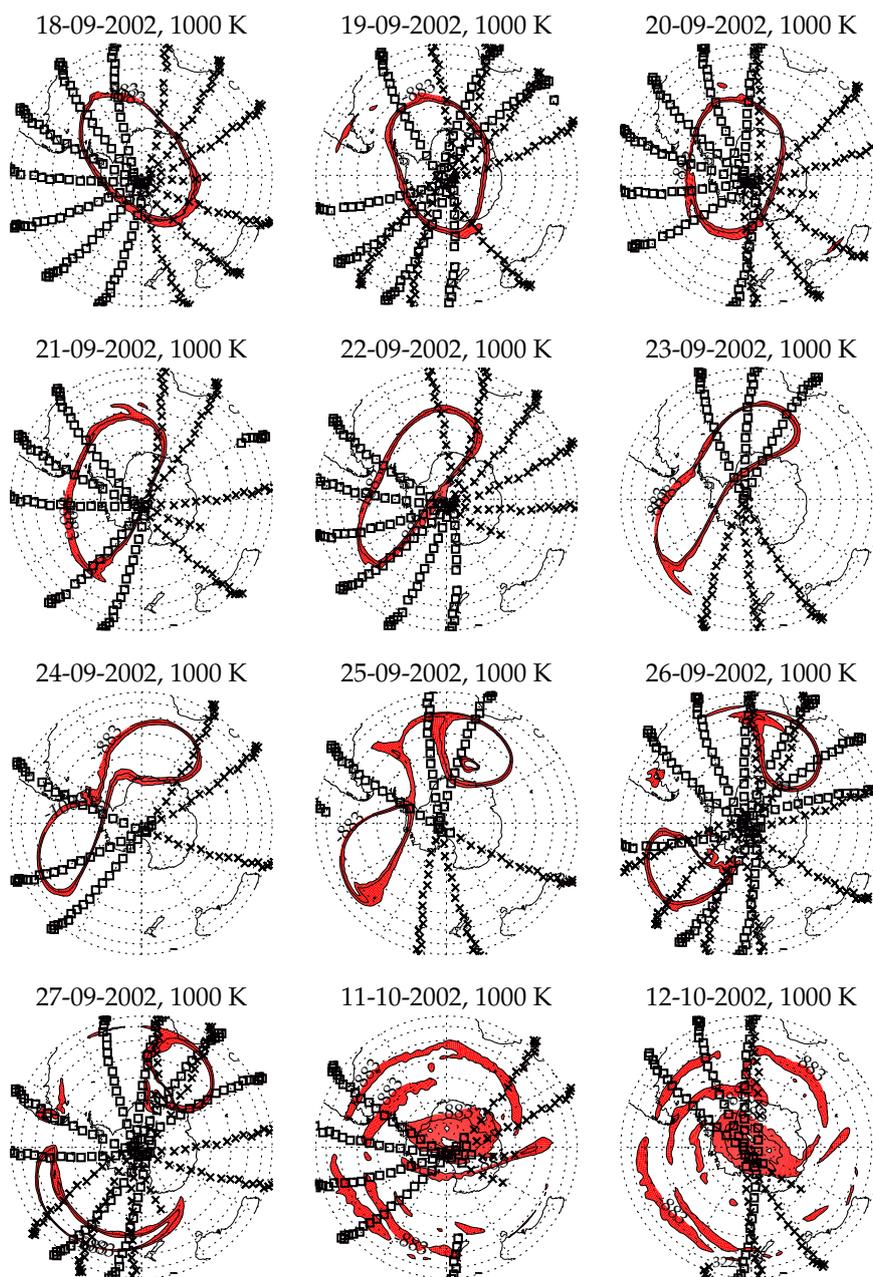
## 2 The Antarctic winter 2002

While some indication of perturbed dynamics had been observed already in the early phase of the Antarctic stratospheric vortex in Austral winter 2002, the vortex behaved more or less as usual from mid-winter up to around 20 September (Figs. 2 and 3). Enhanced ClO in the altitude region between 16 and 23 km gave evidence of chlorine activation (Glatthor et al., 2004). PSCs were observed until 22 September (Höpfner et al. 2004; see Fig. 1), making heterogeneous chemistry possible. In the course of a major warming around 20 September (Allen et al., 2003; Krüger et al.,



**Fig. 1.** Time series of relative PSC coverage (ratio of the number of MIPAS measurements containing a PSC signal and the entire number of measurements) poleward of 55° S at altitudes from 14 to 26 km in September 2002. Since the vertical extent of the instantaneous field of view of MIPAS is about 3 km at the tangent point, the highest altitudes where PSCs occurred can be determined at an uncertainty of 1.5 km. A measurement is considered PSC measurement where the ratio of mean spectral radiances in the interval from 788.2 to 796.25  $\text{cm}^{-1}$  and from 832.3 to 834.4  $\text{cm}^{-1}$  is lower than the threshold value of 4.0 (Spang et al., 2004). Open triangles indicate availability of MIPAS data.

2005; Charlton et al., 2005), planetary waves of wavenumber 1 to 3 (Wang et al., 2005) caused a displacement, deformation, and, at above the 650 K potential temperature level (above approximately 25 km), even a split of the polar vortex. The time of the major warming event coincides with the time of chlorine deactivation via ClONO<sub>2</sub> formation (Höpfner et al., 2004; Richter et al., 2005). During the major warming the vortex was severely weakened above 900 K, leading to excessive mixing of midlatitudinal air into the vortex (Konopka et al., 2005).



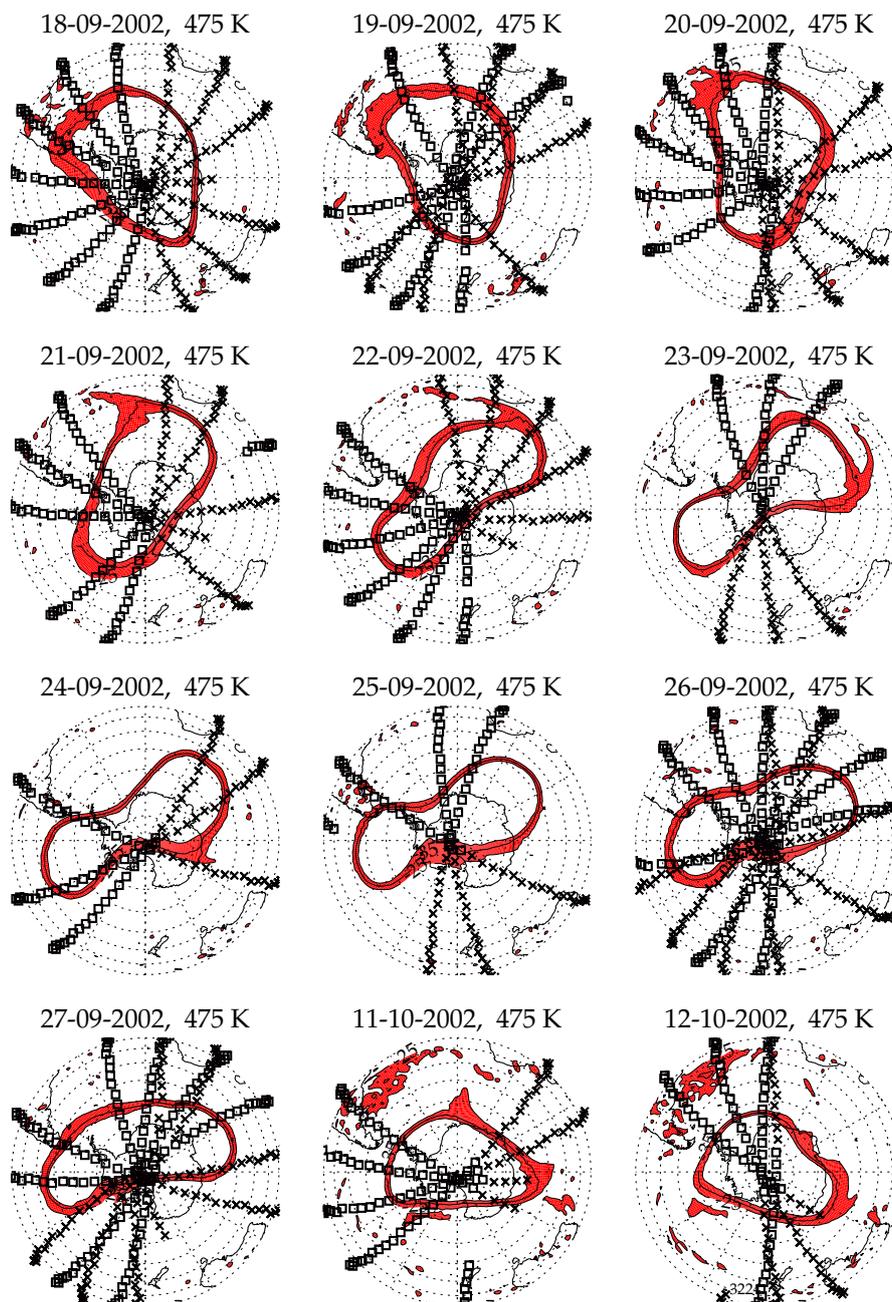
**Fig. 2.** The development of the Southern polar vortex in September 2002 at 1000 K potential temperature based on potential vorticity (PV) data provided by ECMWF. The red belt represents the vortex boundary, defined as  $-1282.6 \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1} < \text{PV} < 855.1 \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1}$ . Open boxes represent the geolocations of the MIPAS daytime measurements, while x symbols represent MIPAS nighttime measurements.

### 3 MIPAS measurements

The data set discussed in this paper was measured with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), which is a limb emission spectrometer designed for measurement of trace species from space (Fischer et al., 2008). It is part of the instrumentation of the Environmental Satellite (Envisat), which was launched into its sun-synchronous polar orbit on 1 March 2002. Data presented here were recorded from 18 September to 27 September 2002

and 11 October to 13 October 2002. The data version used is V2\_HOCl\_2, as described in von Clarmann et al. (2006), where the HOCl data analysis is reported in detail. The precision and total error of a single HOCl profile are estimated at 0.05–0.08 ppbv and 0.05–0.09 ppbv, respectively, at an altitude resolution of about 9 km.

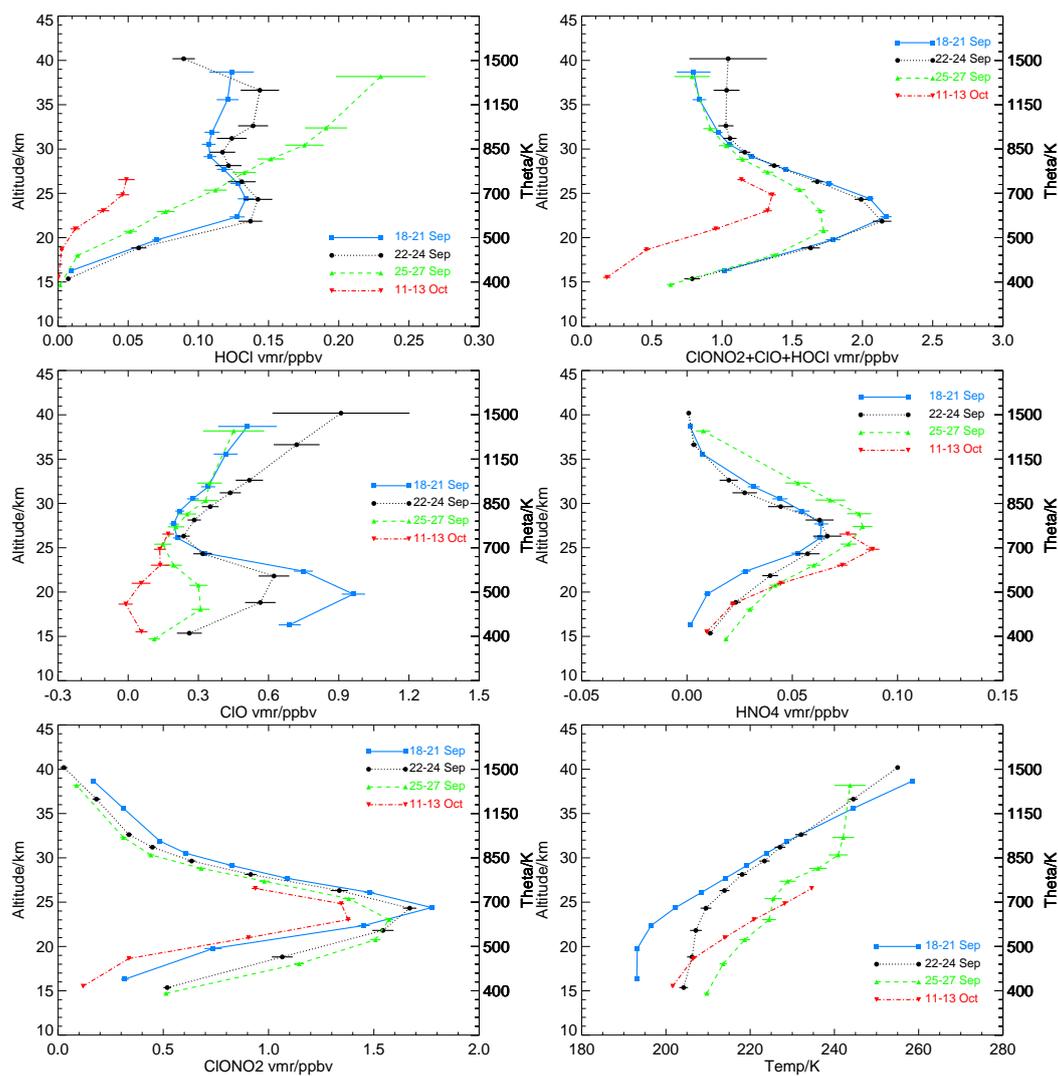
ClONO<sub>2</sub> measurements have been provided by Höpfner et al. (2004). The single profile precision (total error) is estimated at 4–10% (6–11%) at an altitude resolution of 3.3–3.8 km. ClO has been analyzed by Glatthor et al. (2004).



**Fig. 3.** Same as Fig. 2 but for 475 K potential temperature. The vortex boundary region is defined as  $-45.0 \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1} < \text{PV} < -30.0 \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1}$

The single profile precision (total error) in the lower stratosphere is estimated at 19–31% (29–36%) at an altitude resolution of 4 km. ClO mixing ratios measured by MIPAS before 20 September and from 25 September onwards are in agreement with measurements by the Submillimeter Radiometer (SMR) on the Odin satellite (Ricaud et al., 2005). Unfortunately, no SMR measurements have been published for the 22–24 September period.

This study is entirely based on polar vortex averages and their temporal development (Fig. 4). For definition of the vortex edge, a procedure similar to that described by Nash et al. (1996) but with slightly modified parameter settings (Glatthor et al., 2005) was used. This resulted in a threshold of  $-45 \times 10^{-6} \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1}$  at 475-K potential temperature level for vortex air, which is conservative in a sense that the risk that vortex edge air is considered as vortex air is small.



**Fig. 4.** Means of measured Antarctic vortex daytime mixing ratio profiles of HOCl, CIO, and CIONO<sub>2</sub>, (left panels, top to bottom), as well as HOCl+CIO+CIONO<sub>2</sub>, HNO<sub>4</sub> and temperature (right panels, top to bottom) for the periods 18–21 September, 22–24 September, 25–27 September, and 11–13 October. Error bars represent the uncertainties of the mean values in terms of standard deviation divided by the square root of the number of averaged profiles. They include both measurement error and natural variability within the sample. For the HOCl+CIO+CIONO<sub>2</sub> profiles, the CIO and CIONO<sub>2</sub> profiles first were degraded to the HOCl altitude resolution to allow meaningful summation.

Above 700 K, the extrapolation scheme as suggested by Lait (1994) was applied. This resulted in a vortex air threshold of  $-1282.6 \times 10^{-6} \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1}$  at the 1000-K potential temperature level. Potential vorticity data were taken from the T106 ( $1.25^\circ \times 1.25^\circ$  grid) ECMWF analyses.

In order to avoid diurnal sampling artifacts, only daytime measurements (about 10:00 a.m. local time, solar zenith angles smaller than  $94.5^\circ$  to  $95.9^\circ$ , depending on altitude) are considered. In particular, trapping of CIO in the dimer CIOOC1, which is not measured by MIPAS, is negligible then at least for altitudes above about 30 km (Ruhnke et al., 1999b). Error bars of daily or episode mean values are the

statistical uncertainties of the mean values, i.e. the standard errors of the mean. Due to irregular non-random sampling along the Envisat orbits, the actual variability of the atmospheric state within the polar vortex is assumed to be underestimated, because the true standard error of the mean,  $\sigma_{\text{std.err}}$ , depends not only on the standard deviation  $\sigma$  and the sample size  $n$  but also on the average inter-location correlation coefficient  $\bar{r}$ :

$$\sigma_{\text{std.err}} = \sqrt{\frac{\sigma^2(1 + (n-1)\bar{r})}{n}} \quad (1)$$

Since there is no obvious robust way to estimate  $\bar{r}$ , we ignore

it and obtain the usual formulation of the standard error,

$$\sigma_{\text{std.err}} = \frac{\sigma}{\sqrt{n}} \quad (2)$$

and thus underestimate the standard errors of the mean for positive average correlation coefficients, which might be introduced by sampling along Envisat orbits (c.f., e.g. Jones et al. 1997 and references therein for discussion for a slightly different but related problem). As a consequence, the mean profiles do not necessarily represent the entire vortex but may contain local phenomena, and the non-representativeness might not be fully accounted by the standard errors. However, since HOCl, ClO, ClONO<sub>2</sub> and HNO<sub>4</sub> mean values have been obtained from the same observations, direct comparison of these species without sampling artifacts between species is possible.

#### 4 Model calculations

The KASIMA model used in this study is a global circulation model including stratospheric chemistry for the simulation of the behaviour of physical and chemical processes in the middle atmosphere (Kouker et al., 1999; Ruhnke et al., 1999a; Reddman et al., 2001). The meteorological component is based on a spectral architecture with the pressure altitude  $z = -H \ln(p/p_0)$  as vertical coordinate where  $H = 7$  km is a constant atmospheric scale height,  $p$  is the pressure, and  $p_0 = 1013.25$  hPa is a constant reference pressure. A horizontal resolution of T42 ( $2.84^\circ \times 2.84^\circ$ ) has been used. In the vertical regime, 63 levels between 7 and 120 km pressure altitude and a 0.75 km spacing from 7 up to 22 km with a quadratic increase above were used. For the present studies, the version as described in Reddman et al. (2001) is applied, but using ERA-40 analyses up to 18 km, the relaxation term up to 1 hPa and the prognostic part of the model up to 120 km. This version yields realistic mean age of air values (Stiller et al., 2008) as opposed to models using analyses directly (see for example Monge-Sanz et al. 2007).

The chemical module consists of a stratospheric chemistry scheme including all important species belonging to the oxygen, nitrogen, hydrogen, chlorine and bromine families represented by 63 chemical species or families, which are involved in 107 bi- and termolecular reactions, 45 photodissociation and 10 heterogeneous reactions taking place on surfaces of polar stratospheric clouds (PSC) and on liquid sulfuric acid aerosols (Ruhnke et al., 1999a). The existence of NAT and ice is calculated with a thermodynamical approach assuming no supercooling according to the Hanson and Mauersberger (1988) parameterisation for nitric acid trihydrate (NAT) and the Marti and Mauersberger (1993) parameterisation for ice. The rate constants of the gas phase and heterogeneous reactions are taken from Sander et al. (2003). The photolysis rates are calculated online with the fast-j2 scheme of Brian and Prather (2002). In order to allow reasonably large timesteps (6 min) for the integration of production

and loss rates the family concept is applied to  $[O_x] = [O_3] + [O(^3P)] + [O(^1D)]$ ,  $[ClO_x] = [Cl] + [ClO] + 2 \times [ClOOC]$ ,  $[HO_x] = [H] + [OH] + [HO_2]$ ,  $[NO_x] = [N] + [NO] + [NO_2] + [NO_3]$  and  $[BrO_x] = [Br] + [BrO]$ .

The global model runs used in this paper were initialised from a long-term KASIMA simulation on 16 September 2002, 00:00 UT. To simulate as realistic distributions of chemical species inside the polar vortex as possible those trace species which are measured by MIPAS (CH<sub>4</sub> and N<sub>2</sub>O (Glatthor et al., 2005), O<sub>3</sub> (Glatthor et al., 2006), HNO<sub>3</sub> (Mengistu Tsidu et al., 2005; Wang et al., 2007), HNO<sub>4</sub> (Stiller et al., 2007), NO and NO<sub>2</sub> (Funke et al., 2005), N<sub>2</sub>O<sub>5</sub> (Mengistu Tsidu et al., 2004), ClO (Glatthor et al., 2004), ClONO<sub>2</sub> (Höpfner et al., 2004, 2007), HOCl (von Clarmann et al., 2006)) are re-initialised on 17 and 18 September inside the daytime polar vortex with MIPAS daytime averages. As each air parcel is exposed to sunlit conditions during these two days, this procedure leads to a complete re-initialisation of the entire vortex with MIPAS/Envisat data. Re-initialisation of  $[ClO_x]$  is particularly difficult, since this ClO is the only ClO<sub>x</sub> component measured by MIPAS. Re-initialisation of  $[ClO]$  alone while keeping total  $[ClO_x]$  constant does not help because the analytical repartitioning of  $[ClO_x]$  which is implied by KASIMA's family concept would immediately restore the original KASIMA values except for changes related to re-initialised non-ClO<sub>x</sub> species which affect the partitioning. Instead, the total  $[ClO_x]$  was scaled according to MIPAS ClO volume mixing ration (VMR). The goal of re-initialisation is to be able to attribute differences between the measured and the modeled atmospheric state to processes happening during the observed episode.

To ensure comparability and to reduce sampling artefacts, KASIMA vortex averages are calculated for the MIPAS geolocations, after interpolating the model results to these latitudes and longitudes. This approach of matched instead of random sampling (i.e. the use of model output at longitudes and latitudes of the MIPAS measurements) implies that differences between measured and calculated means of mixing ratios can be more significant than the combined standard errors suggest, because the latter have a common correlated sampling component. Since the position of the vortex in KASIMA is not always identical with that of the ECMWF analyses used as a selection criterion for MIPAS measurements, geolocations outside of the KASIMA model vortex have been disregarded.

In order to adjust the altitude resolution of the modeled profiles to that of MIPAS, MIPAS averaging kernels were applied to the model results. MIPAS data used for re-initialisation, however, are by definition provided at the MIPAS vertical resolution. In order to avoid inappropriate double smoothing, the modeled profiles are decomposed into an initial component (18 September data) and a time-dependent component (difference between the actual modeled profiles and the initialisation profiles from 18 September) and the MIPAS averaging kernels are only applied to

the latter component. For some applications where gains and losses of multiple chlorine species are compared, both the measured and modeled data are further degraded to the MIPAS HOCl vertical resolution.

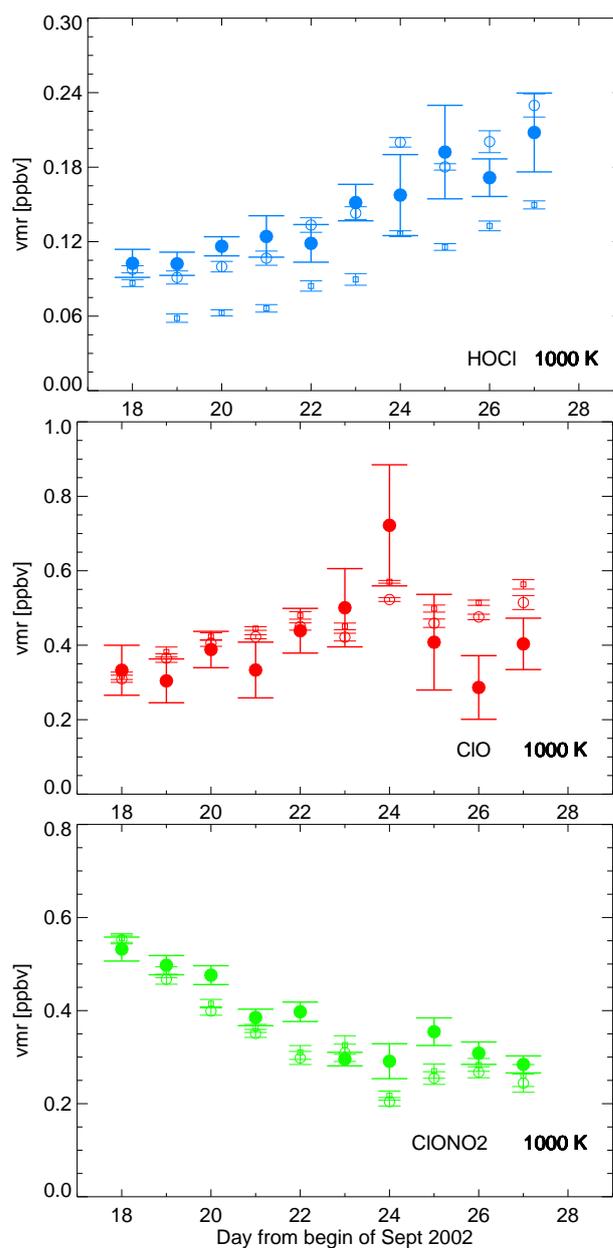
## 5 The temporal development of HOCl, ClO, and ClONO<sub>2</sub> VMR inside the polar vortex

The first available MIPAS data of this data set fall in the period of 18–24 September 2002. MIPAS HOCl measurements for this time are characterized by a pronounced double maximum structure (Fig. 4, upper left panel). First, we discuss the development of the upper maximum above 30 km, which is ruled by gas phase chemistry (Reactions R1–R7). Then, there follows the discussion of the lower stratospheric HOCl maximum which is associated with additional heterogeneous chemistry (Reactions R8–R9). Due to irregular spatial sampling, the temporal development also includes a spatial component and thus cannot be understood as a pure time series.

### 5.1 Gas phase chemistry regime

On 18–19 September the Antarctic vortex still was intact and centered over the South pole. HOCl peak vortex daytime daily mean mixing ratios were found at 33–40 km altitude, reaching approximately  $0.13 \pm 0.03$  ppbv (Fig. 4, top left panel, blue lines). These values are lower than those measured in the midlatitudinal or tropic stratosphere, where peak mixing ratios up to 0.23 ppbv were measured at these altitudes (von Clarmann et al., 2006). This is explained by a reduced availability of HO<sub>x</sub> at polar latitudes (about 40 pptv compared to 150 or 200 pptv at daytime midlatitudes or tropics, respectively, as calculated by KASIMA). Polar vortex daytime mean mixing ratios of ClO were  $0.35 \pm 0.1$  ppbv at 33 km altitude between 18 and 21 September. In polar regions with little sunlight during polar winter, ClO is partly buffered in its reservoir ClONO<sub>2</sub> (Fig. 4, middle left and bottom left panels, blue lines, and Fig. 5, middle and lower panels).

From 20–21 September, the vortex started to be distorted and displaced. During 22–24 September, as the vortex distortion continued during the major warming, ClO mixing ratios increased to values of around  $0.5 \pm 0.2$  ppbv at 33 km (Fig. 4, middle left panel, black lines, and Fig. 5). During these days, a monotonic increase of ClO VMR is observed at all levels above 27 km. This enhancement of ClO VMR was balanced by a reduction of the photochemically unstable ClONO<sub>2</sub> by approximately 0.15 ppbv below ~35 km, while for higher altitudes the source of the excess ClO is not quite clear. During this period, HOCl VMR started to increase. Increasing CH<sub>4</sub> and decreasing CO mixing ratios (appr. 0.3 to 0.4 ppmv and 0.2 to 0.15 ppmv, respectively, at 1000 K) indicate, that the vortex was severely destabilized during the major warming



**Fig. 5.** Time series of HOCl (top panel), ClO (middle panel) and ClONO<sub>2</sub> (bottom panel) daily vortex daytime averages in the polar vortex at 1000 K, corresponding to approximately 33 km altitude. Solid symbols are MIPAS measurements, open symbols are KASIMA calculations. Open circles refer to model calculations with Reaction (R1) rate constants as measured by Stimpfle et al. (1979) (larger HOCl and lower ClO values), while small open squares are model calculations based on the reaction rate as recommended by Sander et al. (2006).

above 900 K, and midlatitudinal air was mixed into the vortex.

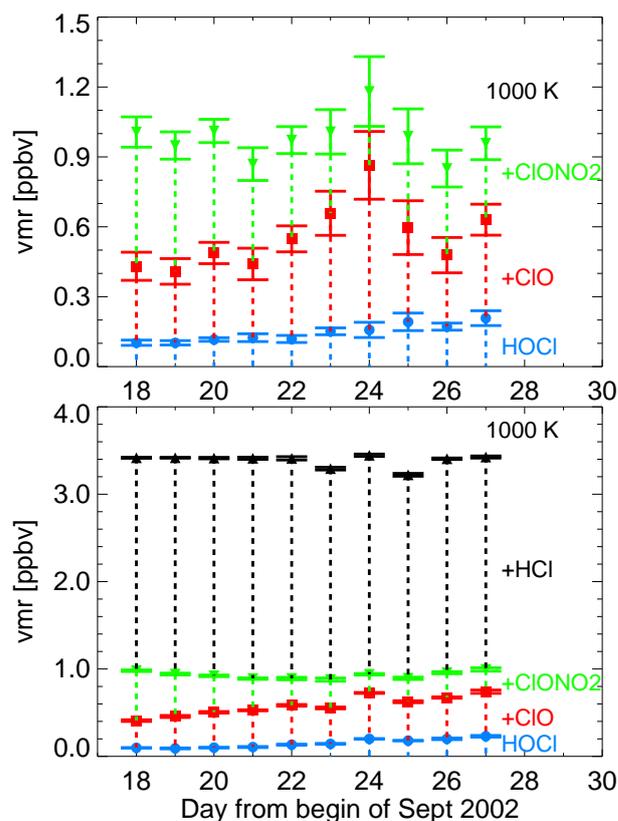
From 24 to 25 September, when the major warming moved parts of the vortex to lower latitudes, measured HOCl vol-

ume VMRs increased rapidly at 1000 K (Fig. 4, top left panel, green lines, Fig. 5). The reason is, that the sounded airmasses were more exposed to sunlight, which triggered more efficient  $\text{HO}_x$  chemistry. The displacement of the vortex to lower latitudes and related exposure to sunlight are even more pronounced in the following days: The exceptionally high HOCl mixing ratios from 25–27 September are explained by midlatitudinal photochemistry, where in particular  $\text{HO}_x$  chemistry is activated, in polar, thus ClO- and  $\text{ClONO}_2$  rich, airmasses. MIPAS measurements of vortex  $\text{HNO}_4$  (Stiller et al. 2007, Fig. 4, middle right panel), which also was observed to increase, support the explanation of accelerated odd hydrogen chemistry.

HOCl mixing ratios outside the displaced and distorted vortex were considerably lower (by approximately 20%). This suggests that the highest atmospheric HOCl mixing ratios are expected whenever polar air is moved towards lower latitudes where enhanced exposure to sunlight increases the efficiency of the HOCl cycle Reactions (R1)–(R4) by the increasing availability of ClO and  $\text{HO}_2$ . While certainly also HOCl loss reactions are more efficient in the presence of sunlight, availability of light causes a net increase of HOCl VMR due to the large amounts of  $\text{HO}_x$  in the sunlit stratosphere.

To analyze the development of the chlorine partitioning, the sum of VMRs of  $\text{ClONO}_2 + \text{ClO} + \text{HOCl}$  was calculated on the basis of MIPAS profiles degraded to the HOCl vertical resolution in order to allow meaningful summation. During the entire period from 18 to 27 September, the VMR of  $\text{ClONO}_2 + \text{ClO} + \text{HOCl}$  was observed to stay approximately constant at about 30 km (Fig. 4, top right panel and Fig. 6), which justifies confidence in the data set. ClO VMR appeared to have increased during 22 and 24 September at the cost of  $\text{ClONO}_2$ , and shows some unexplained temporary high (24 September) and low (26 September) values of which the significance is questionable. At the 1000 K potential temperature level (appr. 33 km altitude) measured VMR of  $\text{ClONO}_2 + \text{ClO} + \text{HOCl}$  seems to have increased on 24 September, due to enhanced ClO VMR. Large overlapping error bars, however, indicate that this increase lacks statistical significance. The significance is even smaller than the error bars suggest since the variability of vortex measurements is underestimated due to non-random sampling given by the Envisat round tracks. HOCl VMR increased continuously from the beginning of the major warming to the end of the measurement period on 27 September (Fig. 5). Unfortunately, in the following phase of the split-vortex event, due to instrument shut-down, no more MIPAS measurements are available. From 11 October on, when MIPAS was operational again, the polar vortex had already dissolved above approximately 28 km altitude, prohibiting further analysis of the vortex airmasses there.

The measured and modeled temporal evolutions of the vortex daytime mixing ratios of the three chlorine species are in reasonable (ClO and  $\text{ClONO}_2$ ) to excellent (HOCl) agreement, when the rate constants proposed by Stimpfle



**Fig. 6.** Measured (upper panel) and modeled (lower panel) temporal development of chlorine partitioning in the polar vortex at 1000 K, corresponding to approximately 33 km altitude. Blue dots indicate HOCl VMRs; red squares indicate the HOCl + ClO cumulative VMR and green triangles indicate the HOCl+ClO+ $\text{ClONO}_2$  cumulative VMR. The lower panel also includes modeled HCl. These model results are based on the Reaction (R1) rate constants by Stimpfle et al. (1979). Error bars refer to the sums, not to the components. All data have been degraded to the vertical resolution of the HOCl retrieval in order to allow meaningful summation and intercomparison.

et al. (1979) are used for Reaction (R1), as proposed by Kovalenko et al. (2007). Using the rate constants of the current JPL recommendation (Sander et al., 2003, 2006) leads to significant underestimation of HOCl amounts. Despite of re-initialisation some discrepancies are observed already on 18 September, because different pressure and temperature profiles in the model and MIPAS data sets cause some ambiguities both in altitude assignment and conversion between mixing ratios and concentrations. The original MIPAS data and averaging kernels are provided as VMR on geometric altitudes, the model is re-initialised on the basis of concentrations, and the vortex mean values are represented as VMR in potential temperature coordinates. Furthermore, there is one time-step of six minutes between re-initialisation and model output.

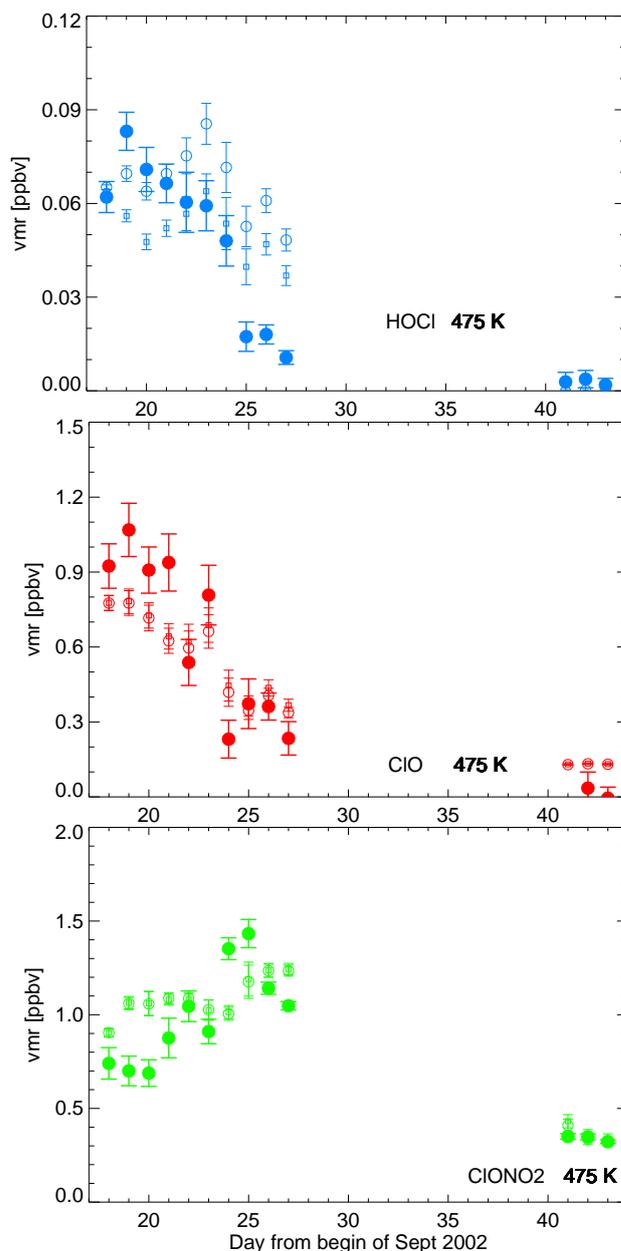
At isentropic surfaces higher than 1000 K only very few MIPAS daytime vortex measurements were available because of the small extension of the vortex at these altitudes then. Therefore, analysis of these data remains somewhat speculative. The destabilisation of the vortex and related mixing during the major warming were even more pronounced at these high altitudes.

## 5.2 Heterogeneous chemistry regime

A lower stratospheric HOCl VMR maximum is visible at approximately 24 km in the 18–24 September data (Fig. 4 upper left panel, blue and black lines). This is an altitude domain, where chlorine activation is driven by heterogeneous chemistry on PSC particles, which also affects HOCl chemistry, either by Reaction (R8) or by Reaction (R1) after heterogeneous ClO formation. Last PSCs were observed by MIPAS on 22 September (Fig. 1). During 16 to 21 September MIPAS has detected some PSCs in the lowermost stratosphere at and below 17–18 km. On 17–18 September a few PSCs have been detected near the Peninsula region at altitudes up to 20–21 km. Höpfner et al. (2006) have attributed occurrence of PSCs in this region to lee-waves triggered by the Peninsular topography. Until 15 September PSCs were detected in MIPAS spectra even at tangent altitudes of about 23 km (Fig. 1). On 13 September high-reaching PSCs covered the largest area.

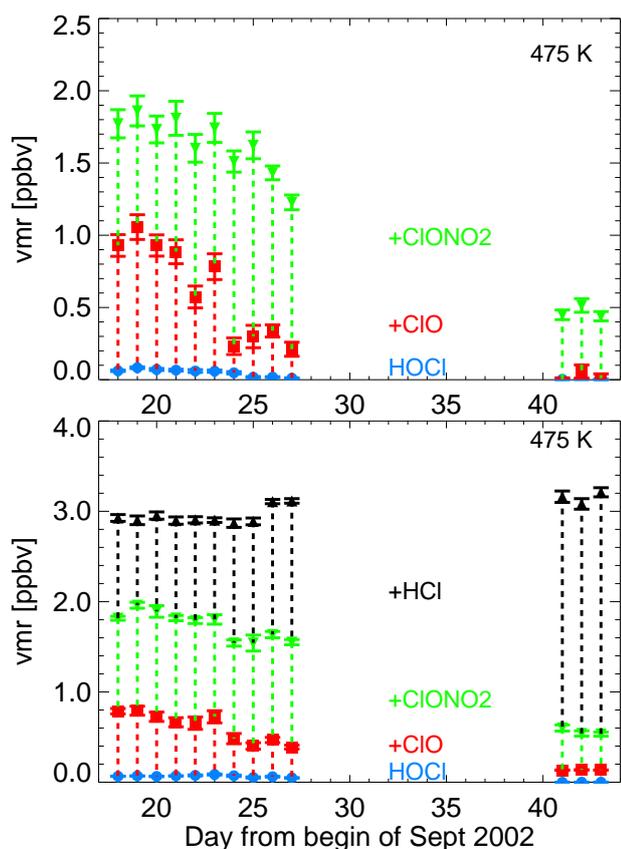
The measured lower stratospheric HOCl maximum on some days slightly exceeded even the upper maximum; daytime daily mean values reached 0.15 ppbv. No substantial variation between 10 a.m. and 10 p.m. measurements was observed here. HOCl mixing ratios were observed to decrease by appr. 5 ppt per day until 24 September at 475 K (Fig. 7, upper panel). From 25 September on, polar vortex mean daytime HOCl mixing ratios were substantially lower (20 pptv). HOCl follows the temporal development of ClO. The rapid ClO decrease from 23 to 24 September goes along with an increase of ClONO<sub>2</sub>. In the October measurements, HOCl, ClO and ClONO<sub>2</sub> VMRs are low due to the usual chlorine deactivation into HCl.

Oscillations in the time series of measured ClO VMR, as well as of HOCl+ClO+ClONO<sub>2</sub>, between 21 and 25 September and the discontinuity in the time series of HOCl between 24 and 25 September are partly attributed to irregular sampling (Fig. 8). This is particularly important since in this time period the vortex was rather inhomogeneous, and varying ozone concentrations led to different chlorine deactivation paths in different parts of the vortex (Groß et al., 2005). Nevertheless, sampling artifacts would not obviously explain the observed time lag between the strong ClO and HOCl decrease on 24 and 25 September, respectively. This time lag suggests that HOCl was substantially destroyed within one day and this loss could not be efficiently compensated by production via Reaction (R1) in an atmosphere with low ClO abundances.



**Fig. 7.** Temporal development of HOCl (top panel), ClO (middle panel) and ClONO<sub>2</sub> (bottom panel) in the polar vortex at 475 K, corresponding to approximately 18 km altitude. For detailed explanation, see Fig. 5.

The rapid HOCl loss mentioned above happened during the vortex displacement, which had caused vortex air masses to be more exposed to sunlight, thus accelerating all three possible loss Reactions (R2), (R6) and (R7) which all depend on sunlight, (R2) as photolysis reaction, (R6) by the illumination-dependent [OH]/[HO<sub>2</sub>] ratio, and (R7) by UV-illumination dependent availability of atomic oxygen. Due



**Fig. 8.** Temporal development of chlorine partitioning in the polar vortex at 475 K as measured by MIPAS (upper panel) and modeled with KASIMA (lower panel), corresponding to approximately 18 km. For detailed explanation, see Fig. 6.

to ongoing ClO-deactivation into ClONO<sub>2</sub> (Fig. 4, middle and lower left panels, c.f. Höpfner et al. 2004), sufficient ClO abundances were no more available to compensate the HOCl loss by any substantial HOCl build up via Reaction (R1). HO<sub>x</sub> abundances as limiting reaction partner of Reaction (R1) can be ruled out, since HNO<sub>4</sub> still was observed to increase (Fig. 4, middle right panel). From 25 September on, HOCl was observed to further decrease in this altitude range, and HOCl measurements on 11–13 October, which represent the Antarctic lower stratosphere after the reformation of the polar vortex, are below 0.06 ppbv and do not differ from the typical global values at these altitudes (c.f. von Clarmann et al. 2006). All this suggests that largest HOCl abundances are to be expected during or immediately after a PSC period in ClO-rich air.

Since PSCs appear in the model run only before 21 September (already reduced to one single occurrence at 50° S, 0° E by then) and not during the rest of the observation period, while still considerable HOCl levels are maintained, the part of HOCl also reproduced by the model must have been generated from previously heterogeneously gener-

ated ClO via Reaction (R1) and not via direct heterogeneous chemistry (Reaction R8). Similar as in the gas phase chemistry regime, rate constants by Stimpfle et al. (1979) result in significantly larger HOCl mixing ratios than those recommended by Sander et al. (2006), which agree better with the 18–21 September MIPAS measurements. Since the HOCl abundance depends that strongly on the rate constants of gas phase Reaction (R1), the assumption of indirect heterogeneous HOCl formation as described above rather than direct heterogeneous HOCl formation via Reaction (R8) is further supported.

During the observation period, the atmosphere was quite warm (above 200 K at 23 km altitude in major parts of the vortex with only a limited area over the Peninsula and Weddell Sea with values of 190–200 K before 23 September), which led to early evaporation of mountain-wave PSCs. Thus, these PSCs were a localized phenomenon, and air was processed only when passing the PSC area, without any possibility of further heterogeneous reaction along the trajectory. The indirectly heterogeneously generated HOCl molecules, i.e. those which are generated via Reaction (R1) from heterogeneously produced ClO, can even be produced when the air parcels contain no more PSCs which could act as an immediate HOCl sink via Reaction (R9).

From 22 September on, modeled HOCl mixing ratios are larger than the MIPAS ones, and the onset of HOCl loss seems to be delayed by about 2–3 days in the model calculation. This is consistent with the earlier decline of PSC occurrence in the model run. The heterogeneous HOCl loss Reaction (R9) was still possible in the real atmosphere while the PSC-free model atmosphere did not allow any heterogeneous reaction any longer. The average HOCl loss rates of MIPAS and KASIMA from 23 to 27 September are quite consistent (about  $-0.01$  ppbv/day). A slight underestimation of ClO mixing ratios along with overestimated ClONO<sub>2</sub> in KASIMA results can also be attributed to ongoing heterogeneous chemistry in the early observation period not reproduced by the model. Poor reproduction of measured ClO values, however, also leaves room for speculation that the quantitative understanding of ClO dimer chemistry is insufficient (von Hobe et al., 2007).

## 6 Conclusions

The temporal development of the HOCl enhancement at 1000 K potential temperature level during the vortex displacement is understood as the triggering of midlatitudinal chemistry through enhanced sunlight in ClO-rich originally polar airmasses. Besides these illumination conditions, also mixing of humid and methane-rich midlatitudinal air into the vortex provided further HO<sub>x</sub> sources, making conditions even more favorable for HOCl build-up. In agreement with Kovalenko et al. (2007), we find that model calculations based on Reaction (R1) reaction rate constants by Stimpfle

et al. (1979) reproduce the measurements better than those based on the current JPL recommendation (Sander et al., 2003, 2006). In the lower stratosphere, large HOCl abundances are attributed to heterogeneous chemistry on PSCs in the Peninsula region, a region where the stratosphere was coldest during this episode, and where in addition lee-waves may play a role. In the observation period, the HOCl abundances were ClO, not HO<sub>x</sub> driven. Air transported through local temperature minima with PSC occurrence, either due to adiabatic lofting above tropospheric weather systems or due to mountain waves, encounters favorable conditions for large HOCl abundances, because after passing the PSC area the air is PSC-free. Thus sink Reaction (R9) has not to be considered further. Moreover, these mountain wave PSCs do not occur directly over the South pole but at latitudes of about 60° S to 70° S, where illumination conditions are more favorable of subsequent homogeneous HO<sub>x</sub> chemistry, which transfers a portion of the heterogeneously generated ClO into HOCl.

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