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HOCl in the Antarctic stratosphere

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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, where HOCl abundances are ruled by gas phase chemistry and at around 24 km, which belongs to the altitude domain where heterogeneous chlorine chemistry is relevant. At altitudes of 33 to 40 km, where in midlatitudinal and tropical atmospheres peak HOCl mixing ratios significantly above 0.2 ppbv (in terms of daily mean values) are observed, 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. 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_x 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 $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$ 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. Comparison with a model run where no polar stratospheric clouds appeared during the observation period suggests that a significant part of HOCl was generated from ClO rather than directly via heterogeneous reaction. Excess ClO and HOCl in the measurements is attributed to ongoing heterogeneous chemistry which is not reproduced by the model. In the following days, a decay of HOCl abundances was observed and on 11 October, polar vortex mean daytime mixing ratios were only 0.03 ppbv.

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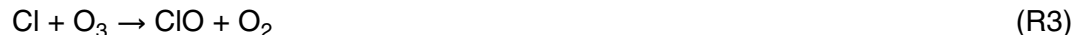
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1 Introduction

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



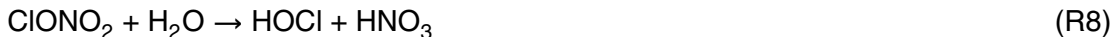
Other HOCl removal reactions are



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:



and further converted to Cl_2 , a precursor of ozone depleting ClO_x radicals, via the heterogeneous reaction



(Hanson and Ravishankara, 1992; Abbatt and Molina, 1992; Crutzen et al., 1992; Prather, 1992).

However, there do not exist many experimental data which can be used to study polar stratospheric HOCl chemistry quantitatively. Midlatitudinal HOCl measurements are

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available from balloon- and airborne infrared solar absorption measurements (Larsen et al., 1985; Toon et al., 1992), space-borne 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 24 km. This enhancement was attributed to heterogeneous chemistry, since polar stratospheric clouds had been observed in advance of these measurements (Höpfner et al., 2004). 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 ClONO₂ (Höpfner et al., 2004) measurements.

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. Enhanced ClO in the altitude region between 16 and 23 km gave evidence of chlorine activation (Glatthor et al., 2004). PSCs were observed until 21 September (Höpfner et al., 2004), making heterogeneous chemistry possible (Fig. 1). In the course of a major warming around 20 September (Allen et al., 2003; Krüger et al., 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 ClONO₂ 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).

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.

ClONO₂ 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). 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. 2). For definition of the vortex edge, a procedure similar to that described by Nash et al. (1996) was used up to the potential temperature level of 700 K. Above, the extrapolation scheme as suggested by Lait (1994) was applied. In order to avoid diurnal

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sampling artifacts, only daytime measurements (about 10 a.m. local time, solar zenith angles smaller than 94.5° to 95.9° , depending on altitude) are considered. In particular, trapping of ClO in the dimer ClOOCl, 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 mean values are the statistical uncertainties of the mean values. Due to irregular non-random sampling along the Envisat orbits, the true variability of the atmospheric state within the polar vortex is assumed to be underestimated. HOCl, ClO and ClONO₂ mean values have been obtained from the same observations. Therefore, 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 T21 ($2.84^\circ \times 2.84^\circ$) 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 an exponential increase above were used.

The meteorology module of the KASIMA model consists of three versions: the diagnostic model, the prognostic model and the nudged model which combines the prognostic and diagnostic model (Kouker et al., 1999). For the simulation of the Antarctic vortex split the nudged model version is used. In this version, the model is nudged towards the operational ECMWF analyses of temperature, vorticity and divergence between 18 and 48 km pressure altitude. Below 18 km the meteorology is based on ECMWF analyses without nudging; above 48 km pressure altitude the prognostic model is used.

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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 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). To simulate as realistic distributions of chemical species inside the polar vortex as possible these trace species which are measured by MIPAS (CH₄ and N₂O, Glatthor et al., 2005; O₃, Glatthor et al., 2006; HNO₃, (Mengistu Tsidu et al., 2005; Wang et al., 2007); HNO₄, Stiller et al., 2007; NO and NO₂, Funke et al., 2005; N₂O₅, Mengistu Tsidu et al., 2004; ClO, Glatthor et al., 2004; ClONO₂, Höpfner et al., 2004, 2007; HOCl, von Clarmann et al., 2006) are reinitialised 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 reinitialisation of the entire vortex with MIPAS/ENVISAT data.

5 The temporal development of HOCl, ClO, and ClONO₂ 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. 2, 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 0.14 ± 0.03 ppbv (Fig. 2, top left panel, blue lines). These values are lower than those measured in the midlatitudinal or tropical 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_x ($[\text{HO}_x] = [\text{OH}] + [\text{HO}_2]$) 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 ± 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_2 (Fig. 2, middle left and bottom left panels, blue lines, and Fig. 3, upper right 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 ± 0.2 ppbv at 33 km (Fig. 2, middle left panel, black lines, and Fig. 3). During these days, a monotonical increase of ClO is observed at all levels above 27 km. This enhancement of ClO was balanced by a reduction of the photochemically unstable ClONO_2 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 started to increase. Increasing CH_4 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 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 volume mixing ratios (VMRs) increased rapidly at 1000 K (Fig. 2, top left panel, green lines, Fig. 3). The reason is, that the sounded airmasses were more exposed to sunlight, which triggered more efficient HO_x chem-

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istry. 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 HO_x chemistry is activated, in polar, thus ClO- and ClONO₂ rich, airmasses. MIPAS measurements of vortex HNO₄ (Stiller et al., 2007) (Fig 2, 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 HO₂. While certainly also HOCl loss reactions are more efficient in the presence of sunlight, availability of light causes a net increase of HOCl due to the large amounts of HO_x in the sunlit stratosphere.

To analyze the development of the chlorine partitioning, the sum [ClONO₂+ClO+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, [ClONO₂+ClO+HOCl] was observed to stay approximately constant at about 30 km (Fig. 2, top right panel and Fig. 4), which justifies confidence in the data set. ClO appeared to have increased during 22 and 24 September at the cost of ClONO₂, 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 [ClO+ClONO₂+HOCl] seems to have increased on 24 September, due to enhanced ClO. 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 because measurements have not been randomly sampled but are interrelated through Envisat ground tracks. HOCl increased continuously from the beginning of the major warming to the end of the measurement period on 27 September

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(Fig. 3). 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.

5 The measured and modeled temporal evolutions of the vortex daytime mixing ratios of the three chlorine species are in reasonable (ClO and ClONO₂) to excellent (HOCl) agreement, when the rate constants proposed by Stimpfle et al. (1979) is 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. While around 20 September modeled [HCl] strongly increases at the cost of [ClO+ClONO₂+HOCl], there is no obvious decrease of the latter species in the MIPAS measurements.

10 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 destabilization of the vortex and related mixing during the major warming were even more pronounced at these high altitudes.

5.2 Heterogeneous chemistry regime

15 A lower stratospheric HOCl VMR maximum is visible at approximately 24 km in the 18–24 September data (Fig. 2 upper left panel, blue and black lines for HOCl). 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. PSCs were observed by MIPAS until 21 September at altitudes above 17 km (Höpfner et al., 2004). Until 15 September
25 PSCs were detected in MIPAS spectra even at tangent altitudes of about 24 km. Figure 1 shows cloud top altitude estimates of 13 September when high-reaching PSCs covered the largest area. From 22 September on, no more PSCs were observed at altitudes higher than 17 km, although MIPAS spectra sampled the Southern polar region

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densely and completely enough such that large areas of PSCs with volume densities larger than $0.3\text{--}0.4\ \mu\text{m}^3/\text{cm}^3$ should have been detected if existent (Höpfner et al., 2006).

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 diurnal variation was observed here. HOCl mixing ratios were observed to decrease by appr. 5 ppt per day until 24 September at 475 K (Fig. 5, upper left 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 ClONO₂. In the October measurements, HOCl, ClO and ClONO₂ are low due to the usual chlorine deactivation into HCl.

Oscillations in the time series of measured ClO, as well as of [HOCl+ClO+ClONO₂] 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 6). 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.

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 Reactions R2, R6 and R7 which all depend on sunlight, Reaction R2 as photolysis reaction, Reaction R6 by the illumination-dependent OH/HO₂ ratio, and Reaction R7 by UV-illumination dependent availability of atomic oxygen. Due to ongoing ClO deactivation into ClONO₂ (Höpfner et al., 2004) (cf. Fig. 2, middle and lower left panels) sufficient ClO abundances were no more available to compensate the HOCl loss by any substantial HOCl build up via Reaction R1. HO_x abundances as limiting reaction partner of Reaction R1 can be ruled out, since HNO₄

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still was observed to increase (Fig. 2, 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 [cf. 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 no PSCs appear in the model run during 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 generated 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). The strong dependence of the modeled HOCl amounts on the related reaction rate rules out that these are large simply due to the reinitialization with MIPAS data on 16 and 17 September. The reinitialization with MIPAS data was necessary because KASIMA underestimated heterogeneous chemistry prior to the observation period, thus heavily underestimating ClO abundances. 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). The strong dependence on the reaction rate of Reaction R1 further supports the assumption of indirect heterogeneous HOCl formation as described above rather than direct heterogeneous HOCl formation via Reactions R8 and R9.

A slight underestimation of HOCl along with large underestimation of ClO in KASIMA can be attributed to ongoing heterogeneous chemistry in the early observation period not reproduced by the model. At altitudes above about 20 km, in mid-September MIPAS observed most PSCs between 60° S and 70° S above the Antarctic Peninsula and in its downwind region. During 16 to 21 September MIPAS has detected some PSCs in the lowermost stratosphere below 17–18 km. On 17–18 September a few PSCs

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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. 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.

6 Conclusions

The temporal development of the HOCl enhancement at 33 km altitude 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_x sources, making conditions even more favorable for HOCl build-up. 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_x driven. Air transported through local temperature minima with PSC occurrence, either due to adiabatic uplifting 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

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60° S to 70° S, where illuminational conditions are more favorable of subsequent homogeneous HO_x chemistry, which transfers a portion of the heterogeneously generated ClO into HOCl. In agreement with Kovalenko et al. (2007), we find that model calculations based on Reaction R1 rate constants by Stimpfle et al. (1979) reproduce the measurements better than those based on the current JPL recommendation (Sander et al., 2003, 2006).

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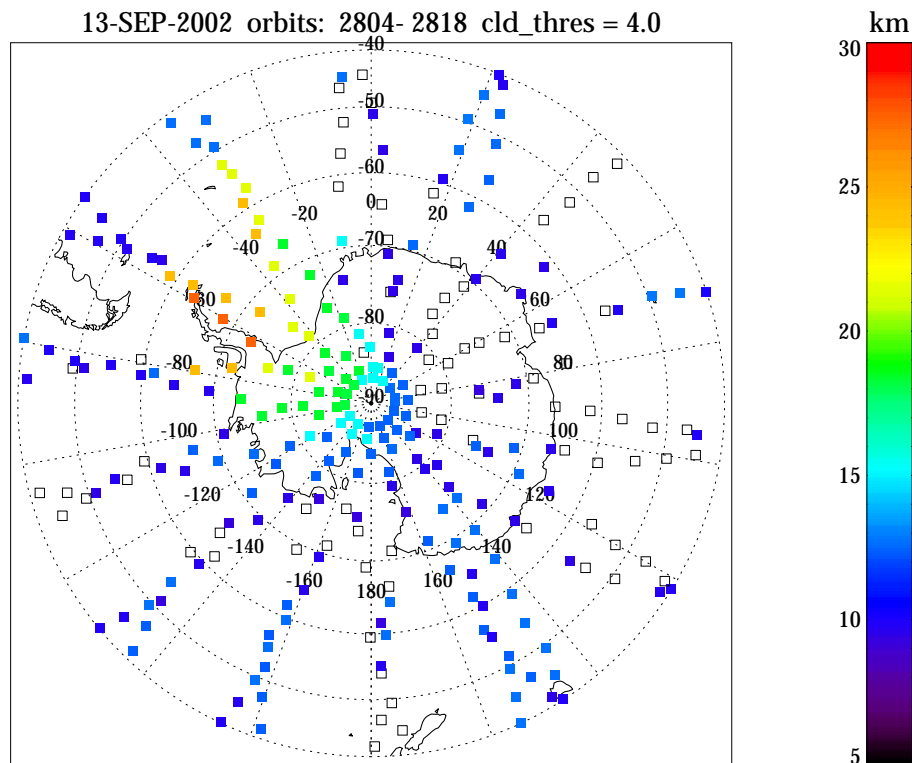


Fig. 1. Highest MIPAS tangent altitudes where the ratio of mean spectral radiances in the interval from 788.2 to 796.25 cm^{-1} and from 832.3 to 834.4 cm^{-1} was lower than the threshold value of 4.0 (Spang et al., 2004) on 13 September 2002. This hints at clouds in a layer of 3 km thickness around the tangent altitude.

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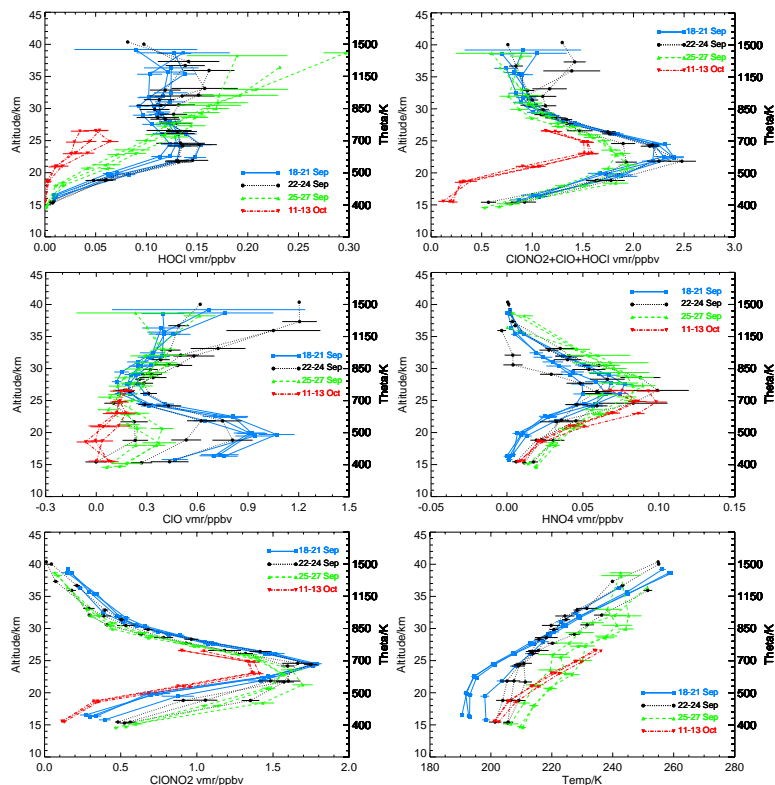


Fig. 2. Daily means of measured Antarctic vortex daytime mixing ratio profiles of HOCl, CIO, and CIONO₂, (left panels, top to bottom), as well as HOCl+CIO+CIONO₂, HNO₄ and temperature (right panels, top to bottom). Error bars represent the uncertainties of the daily means in terms of standard deviation 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+CIONO₂ profiles, the CIO and CIONO₂ profiles first were degraded to the HOCl altitude resolution to allow meaningful summation.

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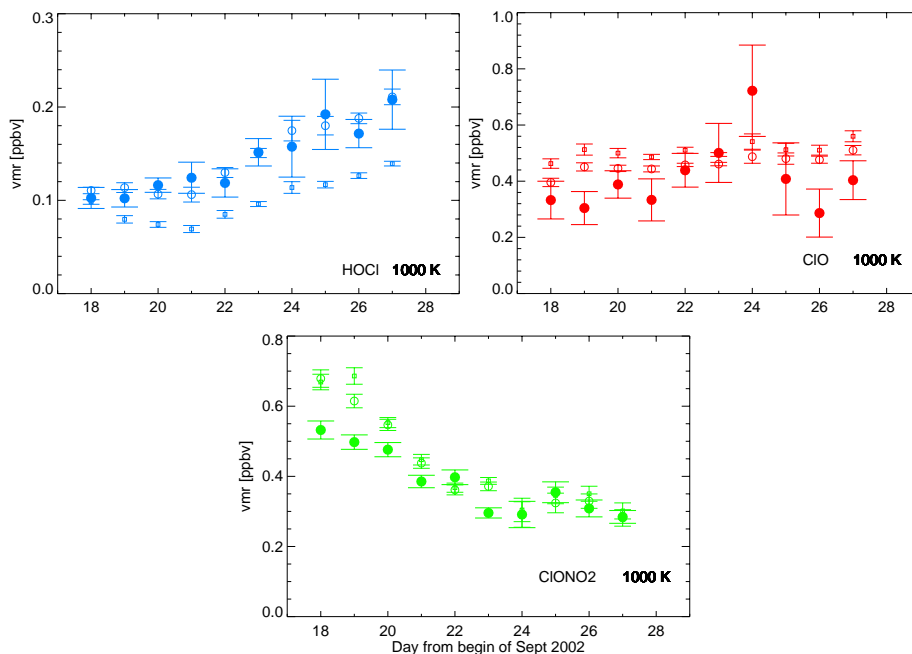


Fig. 3. Time series of HOCl (top left panel), ClO (top right panel) and ClONO₂ (bottom panel) daily vortex daytime averages in the polar vortex at 1000 K, corresponding to approximately 33 km altitude. Solid symbols are MIPAS measurements, open symbols are KASIMA calculations. Open circles refer to model calculations with Reaction R1 rate constants as measured by Stimpfle et al. (1979), while small open squares are model calculations based on the reaction rate as recommended by Sander et al. (2006).

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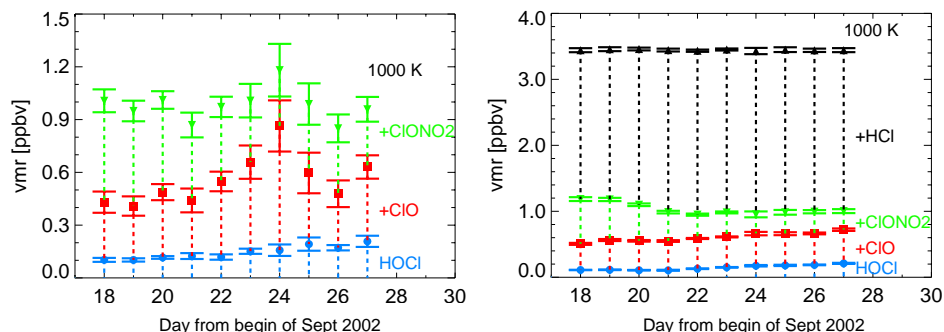


Fig. 4. Measured (left panel) and modeled (right panel) temporal development of chlorine partitioning in the polar vortex at 1000 K, corresponding to approximately 33 km altitude. Blue dots indicate HOCl VMRs; red squares indicate the HOCl+ClO cumulative VMR and green triangles indicate the HOCl+ClO+ClONO₂ cumulative VMR. The right 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.

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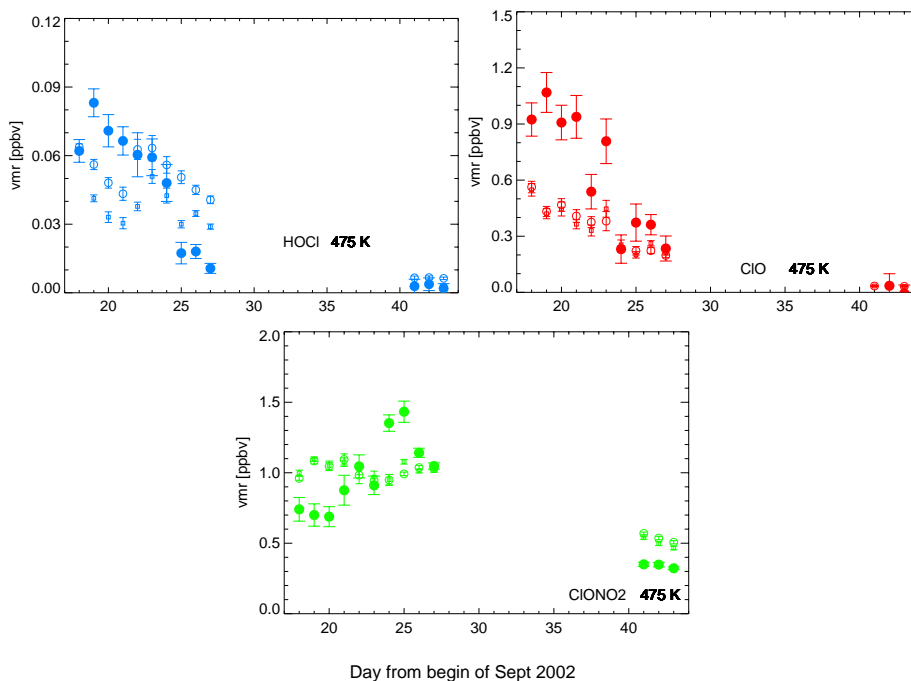


Fig. 5. Temporal development of HOCl (top left panel), ClO (top right panel) and ClONO₂ (bottom panel) in the polar vortex at 475 K, corresponding to approximately 18 km altitude. For detailed explanation, see Fig. 3.

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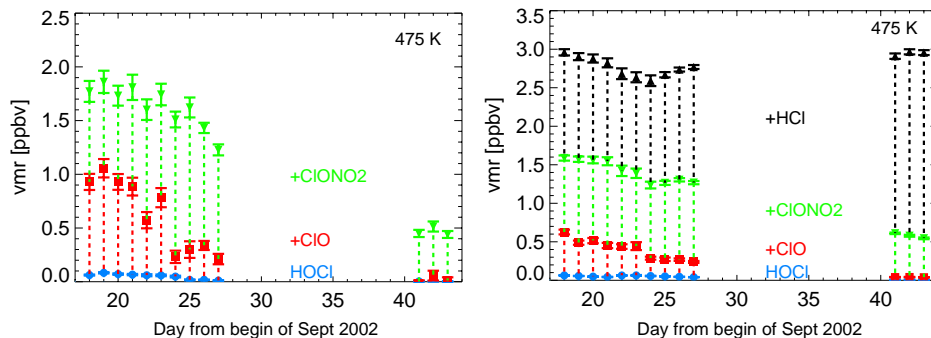


Fig. 6. Temporal development of chlorine partitioning in the polar vortex at 475 K as measured by MIPAS (left panel) and modeled with KASIMA (right panel), corresponding to approximately 18 km. For detailed explanation, see Fig. 4.

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