

Ground based millimeter-wave observations of Arctic chlorine activation during winter and spring 1996/97

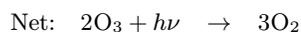
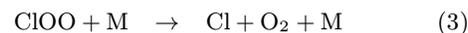
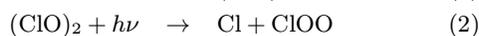
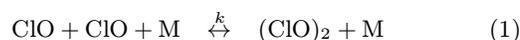
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Abstract. We have performed measurements of stratospheric chlorine monoxide (ClO) in Ny-Ålesund, Spitsbergen (78.9° N, 11.9° E), using a ground-based mm-wave radiometer. In this paper we describe the observed degree of chlorine activation inside the polar vortex in the winter 1996/97. We obtained daily averaged ClO mixing ratios for the lower stratospheric layer on 20 days covering the period from mid-February until the beginning of April. The volume mixing ratio of the lower ClO peak at an altitude of approximately 21 km reached a maximum of 1.6 ppbv. These measurements support the strong chemically induced ozone depletion which was found until April 5 by simultaneous ozone measurements reported in a companion paper [Sinnhuber *et al.*, 1998]. They observed an unusual ozone loss in late April, which corresponds to the observed ClO abundance on April 18-22. On several days we observed diurnal ClO cycles which were compared with model calculations.

Introduction

Anthropogenic fluorochlorocarbons (CFCs) are the major source of chlorine in the stratosphere. The only known relevant natural source of stratospheric chlorine is methyl chloride (CH₃Cl) mainly originating from the world's oceans and burning of vegetation. According to WMO presently more than 80% of stratospheric chlorine is of anthropogenic origin [World Meteorological Organization, 1991]. Approximately 90% of the chlorine is stored in chemically inactive reservoir species such as hydrochloric acid (HCl) and chlorine nitrate (ClONO₂). Under normal stratospheric conditions the active form ClO, shows a single maximum for its volume mixing ratio (VMR) around 40 km of altitude with a relatively small diurnal variation. During the polar winter the temperature inside the polar vortex at around 21 km of altitude can fall below the formation temperature for polar stratospheric clouds (PSC) (approximately 195 K) enabling heterogeneous chemical processes [e.g. Hanson and Mauersberger, 1988; World Meteorological Organization, 1991] to occur on the surface of liquid and solid particles. This process releases large amounts of chlorine from reservoir species. However massive destruction of ozone will not start until

sunlight reappears, because at night ClO is stored mainly in the dimer form (ClO)₂. After sunrise several mechanisms can destroy ozone very effectively. Using a simplified version of the photo-chemical box model BRAPHO (Bremen Atmospheric Photochemical Model) [Trentmann *et al.*, 1997] we have calculated the diurnal cycle of ClO at 21 km for March 13 and 20 considering the following chemical reactions.



All rate coefficients and cross sections were taken from DeMore *et al.*, [1997]. For the calculation of the photolysis frequency of the ClO-Dimer (reaction 2) we used March mean temperatures and pressure profiles from the National Center for Environmental Prediction (NCEP, former NMC) and a mean ozone profile determined from simultaneous mm-wave ozone measurements for March. In Figure 1 calculated ClO profiles for Arctic spring with strong activation of chlorine in the lower stratosphere are presented for day- and nighttime.

Measurement technique and data processing

The Radiometer for Atmospheric Measurements (RAM) is a ground based passive microwave receiver for the detection of thermal emission from molecular rotational transitions in the frequency range 100–300 GHz. The vertical VMR profile of a particular specie can be determined from the information contained in the pressure broadened line shape. For the analysis spectroscopic parameters for the molecule under investigation are needed from appropriate compilations [Pickett *et al.*, 1992]. The system includes two microwave receivers for the detection of ClO at 204 GHz and O₃ at 142 GHz with 1300 K and 3000 K system noise temperature respectively. Both sensors are operated in a time sharing mode using the same acousto optical spectrometer for the real-time spectral analysis of the measured emission lines [Langer *et al.*, 1996]. For ClO observation we use the reference beam method [Parrish *et al.*, 1988], which minimizes instrumental effects such as nonlinearities, and the influence of a rapidly varying troposphere. When retrieving daily mean ClO amounts we improve the spectrum quality by subtracting nighttime from daytime spectra, taking advantage of the large diurnal variation. The total bandwidth of 1 GHz and residual baseline ripples restrict the lower altitude limit to approximately 17 km. An integration

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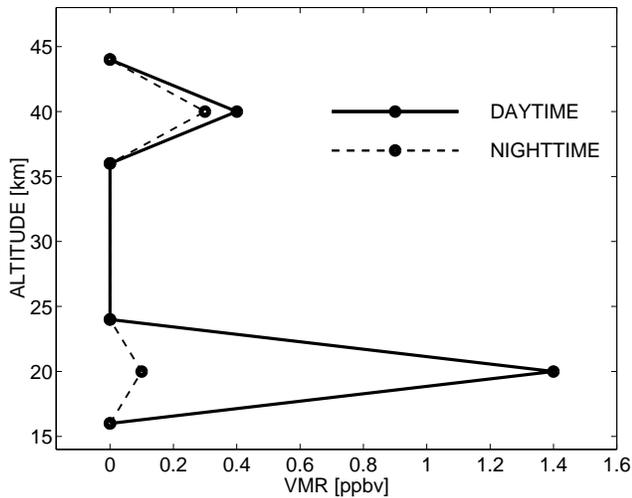


Figure 1. Vertical profile of daytime ClO of March 13 (solid line) for a situation of severely disturbed stratospheric conditions and a typical nighttime profile (dashed line).

time of approximately 100 min is needed to obtain a sufficient signal to noise ratio for day and night measurements. Measurements are restricted to periods of low tropospheric attenuation, usually found under clear and cold weather conditions.

At 21 km altitude a small amount of ClO remains at nighttime, due to thermal dissociation of the dimer. Thus, by subtracting nighttime measurements from daytime measurements we obtain a spectrum that slightly underestimates the daytime ClO signal. Since the amount of ClO remaining at night strongly depends on the stratospheric temperature we do not account for this effect but rather include it in the error budget of our measurements. A reduction of standing waves was achieved by subtracting two sinusoidal waves which have been fitted to the day minus night spectra. The two sine waves were restricted to short periods (typically around 100 MHz with amplitudes of ≈ 30 mK) in order to avoid a detrimental influence on the overall line-shape. The intensity has been corrected for tropospheric opacity and converted to zenith direction (elevation angle 90°). Figure 2 shows a typical day minus night spectrum after the two sine waves have been removed. The solid line is the corresponding radiative transfer calculation using the retrieved ClO profile as input. For the retrieval the model profile as shown in Figure 1 is adjusted by allowing only 4 free parameters to vary, namely the peak mixing ratios and the altitudes for the two maxima in the upper (35–40 km) and lower (16–25 km) stratosphere. The width of the peaks is kept constant at 6 km (FWHM). The retrieved profile is obtained by a best least square fit of the radiative transfer calculation to the day minus night spectrum. The notch in the calculated spectrum is due to nighttime emission of ClO from higher altitudes being stronger than daytime emission.

Results

In contrast to earlier winters when PSCs were observed until February only, the long lasting extremely low temperatures inside the vortex allowed PSCs to occur until the end of March (according to ECMWF data). An analysis of the meteorology of the polar vortex was presented by *Coy et*

al. [1997] and *Sinnhuber et al.* [1998], showing that Ny-Ålesund was located well inside the polar vortex for almost the entire period. Only for a few days around April 12 (day 103) the vortex edge moved over Ny-Ålesund. During the period from mid February to the beginning of April ClO measurements were possible on 20 days covering the whole period with at least one measurement per week. During the remaining time tropospheric opacity was too high for successful measurements. To improve the signal to noise ratio we have integrated all daytime spectra and all nighttime spectra available for a given day and subtracted the two spectra from one another to retrieve averaged daytime profiles. Spectra have been assigned to nighttime if the data were taken at least two hours before sunrise or two hours after sunset. Corresponding daytime spectra were taken at least two hours after sunrise and 3 hours before sunset. This fairly conservative binning is due to the fact that lower stratospheric ClO increases quite rapidly after sunrise and decreases not quite as quickly near sunset [*Emmons et al.*, 1995; *Shindell and de Zafra*, 1996]. The peak VMR values for the lower stratospheric ClO maximum are presented in Figure 3. All measurements were taken inside the polar vortex. A maximum peak VMR of 1.6 ppbv was reached on March 20. For these mean daily values we have calculated the residual of the measured spectra and the best fit. We found an accuracy of 0.2–0.7 ppbv VMR depending on integration time available. The measurement of February 21 (day 52) of 1.3 ppbv agrees with measurements performed by the Microwave Limb Sounder (MLS) observing the highest ClO value in February of about 1.5 ppbv (vortex averaged) on the same day [*Santee et al.*, 1997]. The ClO mixing ratio decreased after the middle of March and was down to almost zero by the beginning of April. After a gap of about 10 days due to bad weather we were again able to take data around April 20 (day 110). Due to the end of polar night no nighttime measurements are possible in late April. Therefore we have used nighttime measurements of April 5 to retrieve mixing ratios. These nighttime measurements were

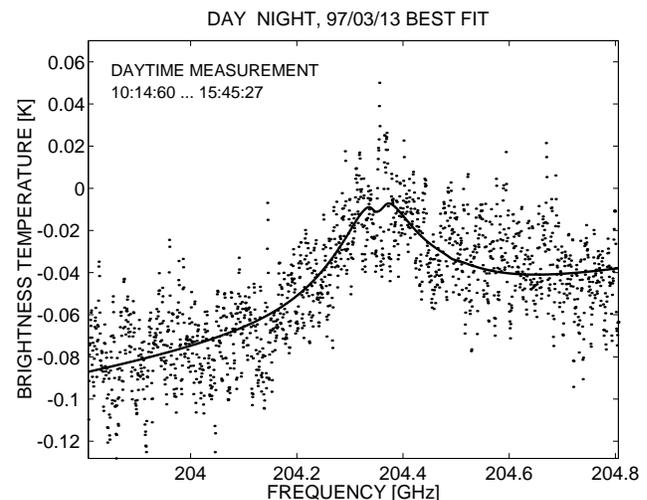


Figure 2. A typical day minus night spectrum with an integration time of ≈ 100 min (day) and ≈ 160 min (night). The intensity is given for zenith direction and has been corrected for tropospheric attenuation. The solid line is a calculated spectrum using the retrieved ClO profile as input.

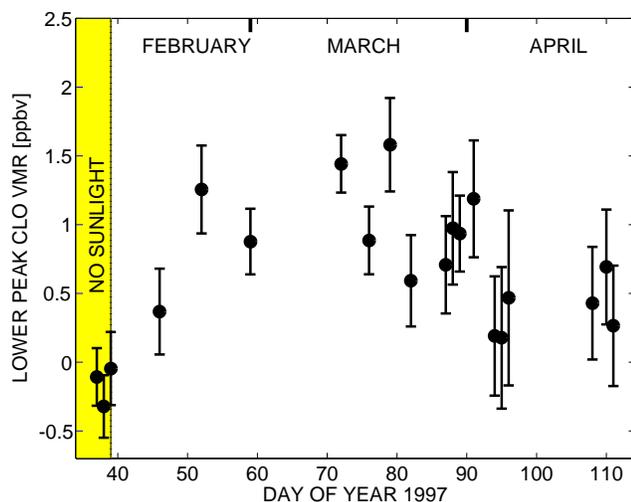


Figure 3. The ClO peak VMRs for the lower maximum near 21 km altitude with 2σ error bars. The shaded area shows the period without sunlight in the stratosphere at 21 km altitude (corresponding to solar zenith angle $< 94^\circ$).

taken at solar zenith angles close to 94° . By subtracting these short-period nighttime spectra we certainly underestimate the mean daytime ClO VMR in late April. However, the late April measurements again show enhanced ClO mixing ratios, although the last possible PSC formation inside the entire vortex (according to ECMWF temperature data) occurred three weeks prior to these measurements. Simultaneous UV/visible measurements performed at Ny-Ålesund showing enhanced levels of stratospheric OCIO (F. Wittrock et al., paper in preparation) support the microwave measurements, since there is no other source for stratospheric OCIO than ClO [Sessler et al., 1995]. Late April ClO enhancement is also supported by ongoing ozone depletion derived from simultaneous ozone measurements [Sinnhuber et al., 1998]. The ozone loss was observed at a slightly lower altitude, at the 475 K (≈ 20 km) isentropic level. Taking into account the altitude resolution of the mm-wave measurements ClO peak mixing ratios (20 to 23 km) and ozone loss were observed in overlapping altitude ranges. However, when MLS measurements were resumed after April 10, no enhanced ClO over Spitsbergen was found (M. Santee, private communication).

From our retrieved profiles we calculated column densities of up to $1.5 \cdot 10^{15}$ molecules/cm² using temperature and pressure data from meteorological radiosondes launched in Ny-Ålesund. Since we have no information on the upper stratospheric ClO peak we only considered the lower maximum of the VMR profiles. The error due to neglecting the ClO above 35 km is less than 4%.

Comparable Arctic ClO columns of up to $1.9 \cdot 10^{15}$ molecules/cm² were calculated from airborne ClO measurements presented by Urban et al. (J. Urban et al., ‘Chlorine activation and ozone destruction in the Arctic winter stratosphere 1996 as measured by the Airborne-Submillimeter-SIS-Radiometer’, paper submitted to GRL) for the winter 1995/96.

Also measurements performed in Antarctica under disturbed stratospheric chemistry [de Zafra et al., 1989] are comparable to the mm-wave data presented in this paper,

considering that the lower stratospheric Antarctic ClO maximum is usually found at lower altitudes than in the Arctic. It should be noted, that ClO column densities retrieved from FTIR observations at Eureka in winter 1997 [Donovan et al., 1997] are larger by a factor of 3–4. However, such large column densities appear not to be compatible with the overall chlorine loading of the stratosphere [World Meteorological Organization, 1991].

On March 13 and 20 the excellent observing conditions allowed the retrieval of ClO data for day and night separately with a temporal resolution of approximately one hour. To estimate the error for this short-term integration we used measurements of February 8 (day 39), because no ClO is expected in the polar night. From this analysis we conclude the accuracy to be better than 1 ppbv. Figure 4 shows the data in comparison with calculations using the BRAPHO photochemical model. The typical day night variation is well matched by the data, giving credibility to both the measurements and the model.

In order to reproduce the ClO measurements we have chosen 2.2 ppbv and 2.25 ppbv of total ClO_x (ClO+2(ClO)₂)

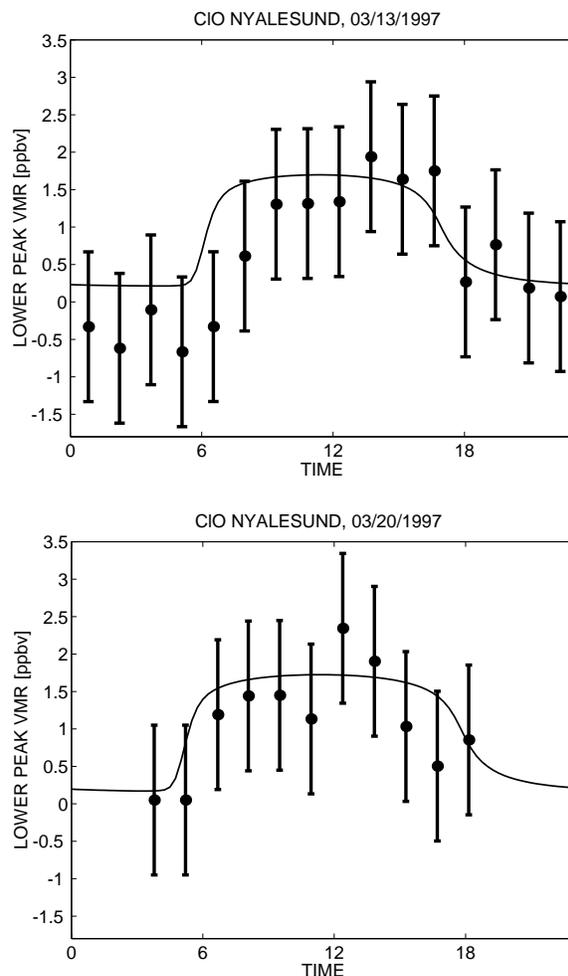


Figure 4. Diurnal ClO variation obtained from the mm-wave data (full circles with error bars). The integration time is approximately 20 min for each measurement. The solid line represents the diurnal variation according to the model calculations for each day.

for March 13 and 20 respectively to initialize the model. According to *World Meteorological Organization* [1991] the upper limit of total inorganic chlorine is considered to be 3.5 ppbv which means that not all the chlorine was converted from the reservoir gases into the active form.

The sharp increase in ClO is due to the very fast photolysis of the dimer after sunrise. The decrease during sunset is slower because the formation of the dimer is of second order in [ClO]. The temporal discrepancy in the onset of the ClO formation between model and measurements on March 13 is due to air masses with different histories observed. Finally we also used the BRAPHO model to calculate the ozone loss due to chlorine chemistry according to the mm-wave measurements. The chemically induced ozone loss was calculated to be of the order of 27 ppbv/day for March. This is a lower limit for the total rate of ozone loss, since other chemical processes are involved as well. From simultaneously performed ozone measurements *Sinnhuber et al.* [1998] have obtained an ozone loss rate of about 22 ppbv/day at the 475 K isentropic level for an averaged twenty days period during March. Taking into account that the latter is a vortex averaged loss rate this is in good agreement with the modeled loss rates for Ny-Ålesund.

Conclusions

We have found high values of stratospheric chlorine monoxide inside the polar vortex during the winter and spring 1997. The maximum ClO VMR measured was 1.6 ± 0.4 ppbv. With respect to the very stable polar vortex we assume that strong chlorine activation occurred from mid February until the beginning of April. Slightly enhanced ClO VMR at the end of April support the unusually late chemically induced ozone loss that was observed by simultaneous ozone measurements in late April [*Sinnhuber et al.*, 1998]. From our measurements we derived diurnal ClO cycles for March. Initializing a photochemical box model with total ClO_x of about 2.2 ppbv for March 13 and 20 we were able to reproduce the ClO measurements. According to this result we conclude that not all stratospheric chlorine was activated. From model calculations we obtained ozone loss rates of about 27 ppbv for March at 21 km. These loss rates are in good agreement with vortex averaged ozone loss rates of about 22 ppbv/day at the 475 K isentropic level during March, derived from simultaneous millimeter wave ozone measurements.

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