Geophys. Res. Lett., Vol. 27, No. 24 , p. 4093-4097, 2000

Winter and Spring Observations of Stratospheric Chlorine Monoxide from Ny-Ålesund, Spitsbergen, in the 1997/98 and 1998/99 Winters

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Abstract. Observations of stratospheric chlorine monoxide (ClO) were performed at the Arctic station of the "Network for the detection of Stratospheric Change" (NDSC). A ground based millimeter wave radiometer was routinely operated in Ny-Ålesund, Spitsbergen (78.9°N, 11.9°E). In 1998 a period with enhanced ClO in a layer around 22 km altitude was detected from February 16 to March 9. Calculations using the three dimensional chemical transport model SLIMCAT are consistent with the observations. In 1999 no significant chlorine activation was observed while SLIMCAT calculations predicted a rather strong chlorine activation in February 1999, when the polar vortex was situated above Ny-Ålesund. Deviations of SLIMCAT calculations for 1999 from the observations could be attributed to differences in temperatures obtained from the United Kingdom Meteorological office (UKMO) used in the model, and temperatures obtained from other sources. UKMO temperatures were compared to temperatures obtained from the National Center for Environmental Predictions (NCEP), the European Centre for Medium Range Weather Forecast (ECMWF) and radio soundings in Ny-Ålesund. A low bias of 1 to 2 K in UKMO temperatures was detected during the preconditioning phase of the vortex air at the altitude were the ClO activation was modeled. No systematic deviation from the radio sonde temperatures were found in the other data sets. In UKMO data temperature differences reach up to 8 K during the investigated time period.

Introduction

A pronounced ozone depletion has been observed over the northern polar region in the winters 1995/96 and 1996/97 [e.g. *Rex et al*., 1997, *Müller et al*., 1997 and *Sinnhuber et al*., 1998]. The major cause for the ozone loss are man made fluorochlorocarbons rising up in the atmosphere and being photo chemically broken up by short wave UV radiation. Fortunately most of the chlorine is stored in the chemically inactive reservoir species chlorine nitrate ($ClONO_2$) and hydrochloric acid (HCl). During the polar night, when the polar vortex forms, the influx of air masses from lower latitudes is suppressed, and the lack of sunlight leads to very low temperatures in the polar lower stratosphere. At a threshold temperature of approximately 193 K at 22 km altitude polar stratospheric clouds (PSCs) can form, providing surfaces for heterogeneous reactions releasing chlorine from the reservoir gases. This threshold temperature critically depends on the water vapor, the nitric acid (HNO_3) and the H_2SO_4 content of the stratosphere [e.g. *Koop et al*., 1997]. The precise formation mechanisms for the different PSC types are not clear yet and are subject of intensive research. However, clear is that small variations in stratospheric temperatures can cause enormous changes in the PSC abundance and the subsequent chlorine activation when temperatures are close to the threshold. Massive ozone loss will only start when sunlight reappears in the preconditioned stratosphere, enabling catalytic cycles to destroy ozone in large quantities. ClO is an indicator for the amount of active chlorine in the stratosphere. The microwave radiometer in Spitsbergen is the only instrument permanently monitoring this important species in the Arctic after the ClO observation frequency of the MLS instrument onboard the Upper Atmospheric Research Satellite (UARS) was severely reduced.

Measurement technique and data processing

The Radiometer for Atmospheric Measurements (RAM) consists of three microwave receivers for the detection of emission lines of stratospheric water vapor at 22 GHz, ozone at 142 GHz and ClO at 204 GHz. For a detailed description of the instrument we refer to *Langer et al*. [1996]. The ClO receiver has an instantaneous bandwidth of 1 GHz at a frequency resolution of 1.5 MHz. The ClO emission is extremely weak and all possible measures to suppress instrumental and tropospheric effects have to be taken. We employ the reference beam technique for the observations [*Parrish et al*., 1988]. In addition we take advantage of the strong diurnal variation of ClO in the lower stratosphere and subtract night time measurements where almost no ClO is present in the lower stratosphere from day time measurements [e.g. *de Zafra et al*. 1989].

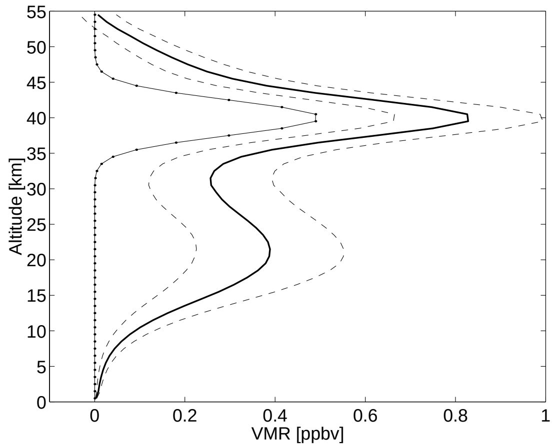

Figure 1. ClO profile of March 8, 1998 (solid line). The dashed lines indicate the error of the retrieved profile. Below 17 km the result starts to be dominated by the a-priori profile used in the retrieval process (solid dotted line). Above 30 km the day minus night differencing might not be applicable, and the profile can be inaccurate.

The altitude profile of a given species is retrieved from the pressure broadened line shape of the measured rotational emission line. The retrieval algorithm is based on the optimal estimation method (OEM). Residual instrumental effects and the total bandwidth limit the lowermost altitude layer where ClO profiles can be retrieved to ~17 km. Below this altitude the result starts to be dominated by the a-priori profile used in the retrieval process. The uppermost layer of 30 km is

determined by the diurnal cycle of ClO. The day minus night differencing does not necessarily lead to meaningful results at higher altitudes where ClO has a weaker diurnal cycle.
In the day minus night time differencing process, day time is defined as 2 hrs after sunrise to 3 hrs before sunset in the stratosphere or the 2 hrs around local noon when the day is too short for this condition. Correspondingly night time is defined from 3 h after sunset to 1 h before sunrise. Using the difference between all integrated day and night time spectra we have retrieved daily averaged midday mixing ratios. In Figure 1 the ClO profile of March 8, 1998 (solid line) is shown. The solid dotted line represents the a-priori profile used in the retrieval process. The dashed lines indicate the error of the retrieved profile as derived from the OEM calculation where the spectral noise and an error for base line effects were introduced in the spectrum covariance. The a-priori covariance was set to 1 ppbv over the complete altitude range.

Meteorological situation

Since stratospheric temperatures show a strong year to year variability in the Arctic, the chlorine activation also varies substantially from year to year. The winter seasons 1997/98 and 1998/99 were rather warm compared to the two previous

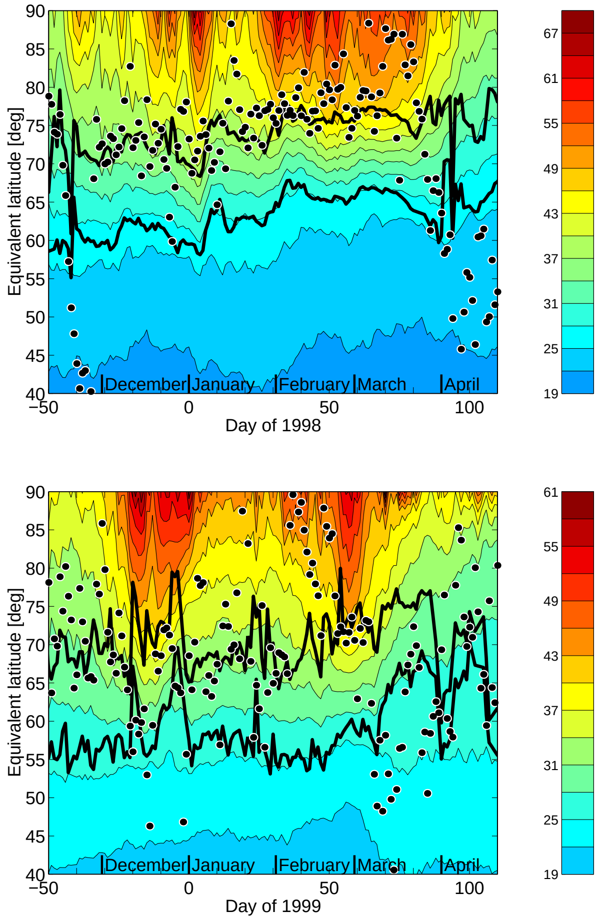

Figure 2. Potential vorticity (PV) versus time and equivalent latitude from November 11, 1997 to April 20, 1998 (upper panel) and from November 11, 1998 to April 20, 1999 (lower panel). The thick solid lines indicate the inner and outer edge of the polar vortex, full circles indicate the position of the observation site, Ny-Ålesund.

winters when a rather strong chlorine activation was observed [e.g. *Santee et al*., 1997 and *Raffalski et al*., 1998]. Considering 193 K to be the threshold temperature for the formation of Type I PSCs around 22 km altitude (~32 hPa) these PSCs were possible inside the vortex almost throughout the whole period from December 1997 to the end of February 1998, according to the ECMWF analysis. A short period with temperatures below 187 K allowing Type II PSC formation appeared at the end of January and the beginning of February.
In 1999 minimum temperatures inside the polar vortex at 22 km altitude were below 193 K only at the end of January and the beginning of February, and never below 187 K, again according to the ECMWF analysis.
In Figure 2 the potential vorticity (PV) versus time and equivalent latitude from November 11, 1997 to April 20, 1998, and from November 11, 1998 to April 20, 1999 are shown. The solid lines indicate the inner and outer edge of the polar vortex according a definition based on the PV-gradient [*Nash et al.* 1996], full circles show the position of the observation site, Ny-Ålesund. It is evident from the maximum PV values that compared to previous years the vortex was rather weak in 1997/98 and even less pronounced in 1998/99. In 1997/98 Ny-Ålesund was located inside the vortex from the beginning of December until mid March. In particular during the period of very low stratospheric temperatures around day 50, Ny-Ålesund was clearly located inside the vortex. However in 1998/99 the vortex was smaller and less pronounced (smaller PV values and smaller PV gradient versus equivalent latitude) than in 1997/98. Ny-Ålesund was frequently located outside of the vortex, and the vortex was less stable than in 1998/99. For the period with the lowest stratospheric temperatures Ny-Ålesund was located in the edge region of the vortex from day 20 to 30, inside the vortex from day 31 to 50 and again in the edge region until day 55.

Results

Nineteen days of favorable weather conditions for microwave observations of ClO were available in 1998, covering the period between February 6 and April 6. In Figure 3 we show the RAM observations at 22 km (~32 hPa) (solid circles with error bars) along with data from the Microwave Limb Sounder (MLS) onboard UARS (crosses with error bars), in comparison with an updated multi-annual run of the 3-d chemical transport model SLIMCAT [*Chipperfield*, 1999]. ClO VMRs were modeled for 12:00 UTC. It is important to note that MLS data are presented as an average over the area from 75 to 85°N and 0 to 30°E, and have been retrieved for a 5 km thick layer centered at 32 hPa (*M. L. Santee, personal communication*). The MLS VMRs were obtained around local noon and have been offset by half a day for clarity. The spatial range observed by RAM and MLS are comparable since the RAM observations represent an average over the integration time of approximately 3 hrs. During this time an air parcel covers a distance of 130 km assuming a typical wind speed of 12 m/s in the stratosphere. This is approximately one fourth of the area over which the MLS observations were averaged in east-west direction. Spatial differences in other than the wind direction can not be accounted for. The altitude resolution of the MLS profiles is slightly better than of the RAM observations which might lead to slightly higher maximum VMRs in the MLS profiles. Observations of MLS and RAM agree within the error bars. A slight but significant chlorine activation was observed in the two data sets as well as in the SLIMCAT calculations after day 50. The SLIMCAT calculations have been degraded to the altitude resolution of the RAM profiles (solid line) and are also shown in their original resolution (dotted line). The onset of the activation predicted in the model calculations was not covered by the RAM due to bad weather, and MLS was not pointing north during this period. The ClO activation in SLIMCAT calculations agrees with the observations within the error of the measurements. The ClO activation in mid February 1998 is confirmed by strong vortex averaged

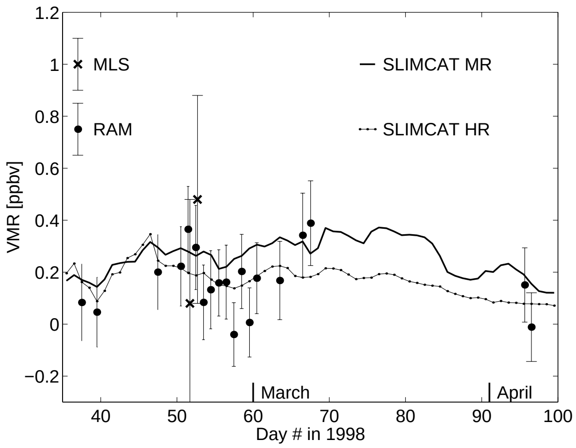

Figure 3. ClO volume mixing ratio at 22 km (~32 hPa) altitude above Ny-Ålesund from February 6 to April 9, 1998. Solid circles with error bars represent the RAM measurements. Crosses with error bars represent measurements of the MLS instrument. The solid and the dotted line represent the ClO VMR calculated by the SLIMCAT model degraded to the RAM altitude resolution (MR) and in the original resolution (HR).

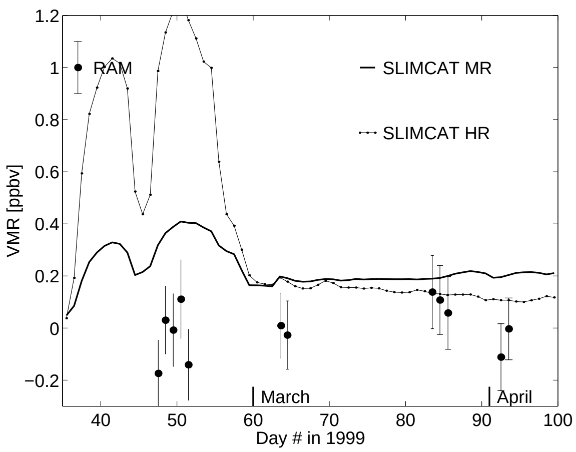

Figure 4. Same as Figure 3 for 1999 without MLS observations.

chemical ozone loss at the same time observed by *Langer et al.* [1999].

In 1999 we had 12 days of favorable weather condition for ClO observations in Ny-Ålesund. In Figure 4 we show the same as in Figure 3 but for 1999. The large difference between the degraded and original SLIMCAT profiles for this year are due to the very special shape of the modeled ClO profiles. Enhanced levels of ClO were modeled for a very narrow layer of only 4 to 5 km thickness around 22 km altitude (~32 hPa). This thin layer is smoothed out in the degradation process. In 1999 no chlorine activation was observed although the model predicts a rather strong activation coincident with low vortex minimum temperatures obtained from ECMWF and UKMO from day 35 to 59. This is not only in contrast to the ClO observations but also to the results of MATCH, an experiment that uses ozone sondes to calculate chemical ozone loss along trajectories. *Schulz et al.*, [2000] found no ozone loss for the winter 1998/99. No coincident MLS measurements were available for this winter. The rather large differences between modeled and observed ClO in 1999 can be understood by the temperature data used in the model calculations. We have compared stratospheric temperatures obtained from UKMO, ECMWF, NCEP to local radio sonde observations at Ny-Ålesund. The comparison has been carried out on the UARS pressure levels on which the UKMO data were assimilated for the period between December 1998 and April 1999. Pressure was interpolated logarithmically to the UARS pressure levels and temperature was interpolated linearly when necessary. Only data pairs with a time difference smaller than 1 h were compared. The results are summarized in Table 1 for the investigated pressure levels. Down to a pressure level of 32 hPa all data sets agree statistically quite well with mean differences below 0.5 K to the sondes. At lower pressures NCEP and ECMWF deviate significantly. It is evident that UKMO data show the largest standard deviation. Since UKMO temperatures were used for the model run we have plotted in Figure 5 UKMO and sonde temperatures and their

Table 1. Mean difference and standard deviation between temperatures derived from local radio sondes and meteorological data centers at Ny-Ålesund.

Pressure [hPa]	Sonde - UKMO [K]	Sonde - NCEP [K]	Sonde - ECMWF [K]
147	0.28 ± 1.28	0.22 ± 1.08	-0.03 ± 1.08
100	0.17 ± 1.29	0.38 ± 0.77	-0.17 ± 0.83
68	0.28 ± 1.40	0.01 ± 0.60	-0.20 ± 0.94
46	0.47 ± 1.62	-0.01 ± 1.05	0.11 ± 0.96
32	-0.32 ± 1.63	-0.25 ± 0.80	-0.08 ± 1.42
22	-0.27 ± 1.68	-1.40 ± 1.40	-0.01 ± 1.73
15	0.44 ± 2.00	-1.25 ± 1.80	1.63 ± 2.84

difference versus time for a part of the investigation period. The largest differences of up to 8 K occurred around day 60 when the polar vortex moved away from Ny-Ålesund (see also Figure 2) followed by a strong temperature gradient. This feature is not evident in the other two data sets. The possible cause for the ClO over-prediction of the model is the uninterrupted low bias of 1 to 2 K on the 32 hPa level between day 28 and 55. This bias is also not evident in the other data sets and on other pressure levels of the UKMO data. This exactly happens in the period with the lowest stratospheric temperatures above Ny-Ålesund, when the model predicted the chlorine activation. Although the bias appears very small it is critical because the temperature was very close to the threshold temperature of Type Ia PSC formation (NAT). Additionally the uptake coefficient of chlorine nitrate in liquid aerosols (Type Ib PSCs) is extremely temperature dependent at these temperatures [*WMO*, 1998]. Thus small variations of the temperature in 1999 can cause very large changes in the chlorine activation, while temperatures in 1998 were clearly below the threshold and rather uncritical. The authors are aware that this temperature comparison might not necessarily be representative for the whole polar vortex where chlorine

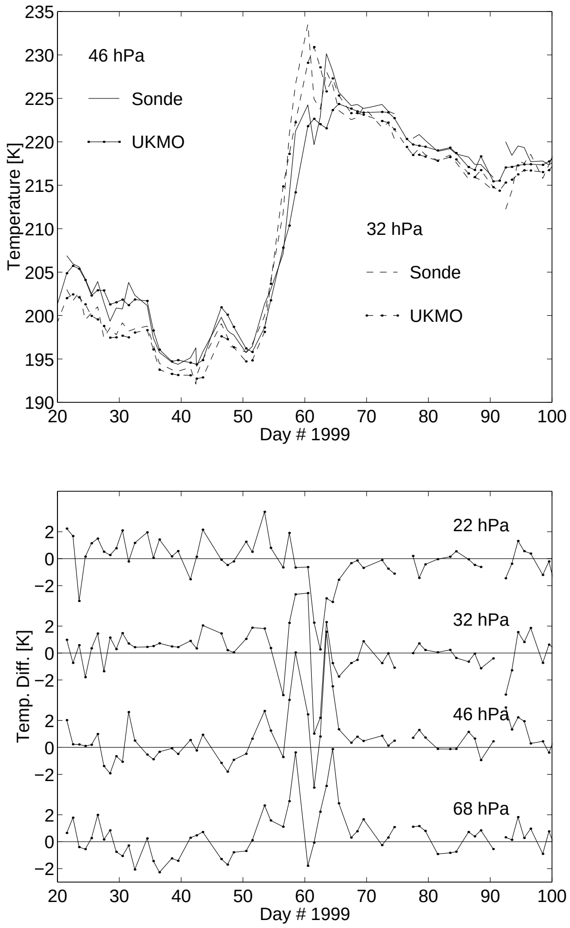

Figure 5. Upper panel: UKMO temperatures used in the model and sonde temperatures at 32 and 46 hPa. Lower panel: Differences between UKMO and sonde temperatures at Ny-Ålesund (sonde – UKMO) at 4 pressure levels between January 21 and April 10, 1999.

activation can occur. Nonetheless this temperature difference provides a strong indication for the origin of the deviations between measurements and the model calculations of ClO.

Conclusions

We have made observations of stratospheric chlorine monoxide at the high latitude site Ny-Ålesund. In February 1998 a significant chlorine activation was found and the SLIMCAT model captured this activation phase. In 1999 we did not observe any significant chlorine activation while the model predicts a rather strong activation phase in February. The differences in 1999 can be attributed to a low bias in the stratospheric temperatures used in the model. Modeling of chlorine activation with no accurate knowledge of stratospheric temperature and the precise PSC formation mechanisms appears to be very critical especially around the PSC formation temperature.

Acknowledgements: We thank M. L. Santee for kindly providing the MLS data and M. Chipperfield for providing the SLIMCAT data. We also thank the ECMWF, the NCEP and the UKMO for providing the PV and temperature data. This work has been supported by the Alfred-Wegener-Institute for Polar and Marine Research and the German Ozone Research Program of the ministry for education and science (Project no. 01 LO 9528/8).

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