7 Results of the OClO measurements

During the last decade OClO in the stratosphere has been measured with ground based instruments by several groups [Solomon et al., 1987a; Fiedler et al., 1993; Schiller et al., 1990; Van Roozendael et al., 1995; Gil et al., 1996; Kreher et al., 1996; Otten et al., 1998; Friess et al., 1998]. Although from these measurements many important findings have been derived, they suffer from three major restrictions.

A) Restricted temporal coverage for vortex air:
Ground based measurements can only provide time series of the OClO absorptions for specific locations which are often situated at the edge of the polar vortex (like e.g. Kiruna). Thus the time series can provide OClO data related to 'ozone hole chemistry' only for the days when the vortex is above the measuring site (For Kiruna this is the case for about 50% of the observations [Otten et al. 1998; Enell et al., 1998].

B) Comparisons for different locations are difficult:
Since the atmospheric OClO absorptions are very small (typically only a few per mil) relatively large statistical but also systematic errors result (see section 4.3.8). Thus it is difficult to perform a comparison of OClO data derived from different instruments at different locations, e.g. in both hemispheres.

C) No total OClO SCDs are measured:
OClO observations are important during polar winter/spring when stratospheric ozone destruction takes place. However, for measurements at high latitudes during winter the daily maximum elevation of the sun is rather low. Thus the OClO absorption in the Fraunhofer reference spectra can be not neglected and the OClO results of a DOAS fitting procedure is rather small, because of the small difference in the SZAs. Due to this effect the ground based OClO data during mid winter typically show relatively large uncertainties or even systematically underestimate the OClO absorptions compared to measurements made during spring.
GOME is the first satellite instrument which measures OClO in the atmosphere. Thus it is now possible to observe the OClO absorption over extended areas including e.g. large parts of the polar vortices. In particular the atmospheric OClO absorptions can be measured with one instrument using one OClO algorithm for different locations. Thus these results can be compared directly which is in particular important for the comparison of the chlorine activation in both polar regions.
A further important advantage compared to ground based observations is that it is possible to determine total atmospheric OClO SCDs instead of differential SCDs (see section 4.3.8).
One restriction of the GOME observations is that the SZA for an individual observation is a function of season and location which has to be taken into account when GOME observations are used for the study of atmospheric bromine and chlorine chemistry (see below).

In the following sections we first give an overview about the GOME observations of OClO related to stratospheric chemistry (section 7.1 to 7.3). We compare the satellite measurement to ground based observations and describe the evolution of the chlorine activation in both hemispheres from the start of ERS-2 in April 1995 to the present.
In section 7.3 we determine an upper limit for the OClO concentrations in the boundary layer for an event of enhanced BrO concentrations.

7.1 OClO in the Stratosphere

7.1.1 General features, SZA dependence

In Figure 7.1 the OClO SCDs for two GOME orbits of 19.01.1997 are shown as a function of the latitude and the corresponding SZA. On this day the polar vortex was largely displaced with respect to the geographic north pole and in consequence some orbits are situated completely outside and others inside the polar vortex (see Figure 7.2). The two orbits selected in Figure 7.1 are examples for both cases, respectively.

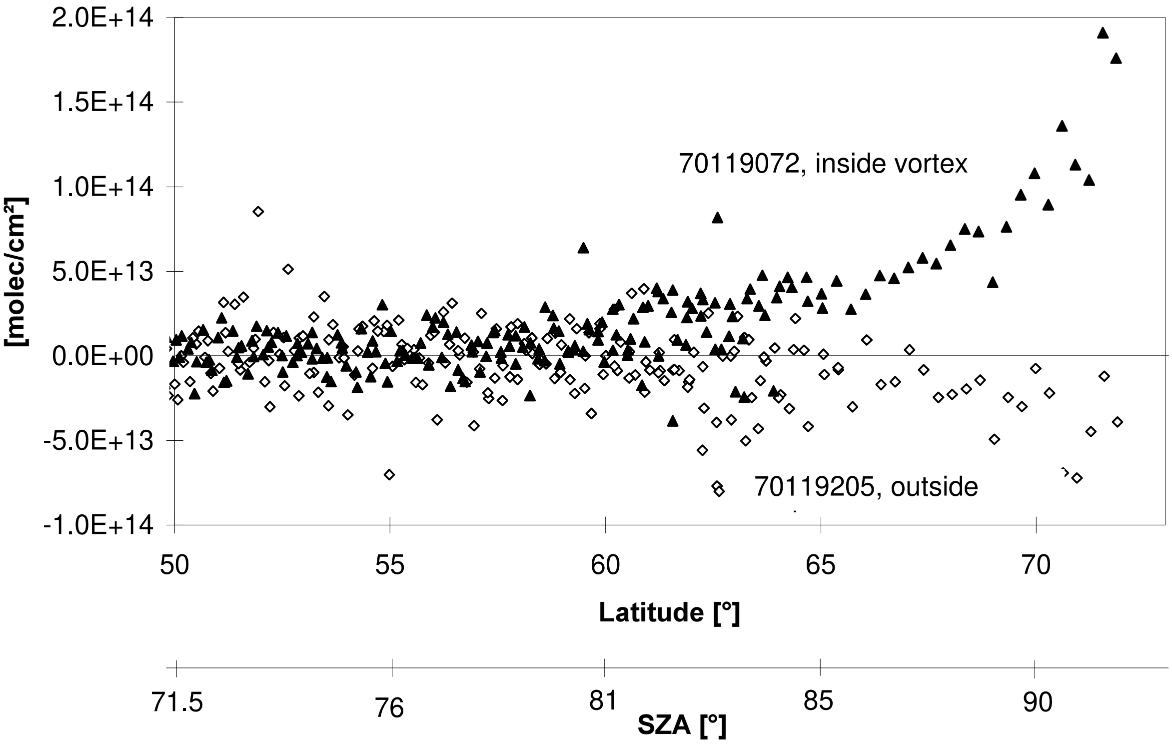


Figure 7.1 OClO SCD for two different orbits on 19.01.1997 as function of latitude. One orbit was completely outside the polar vortex, the other partly inside (see Figure 7.2). OClO was detected only inside the polar vortex (orbit 70119072). The lower x-axis shows the approximate SZA corresponding to the latitude range on that day.

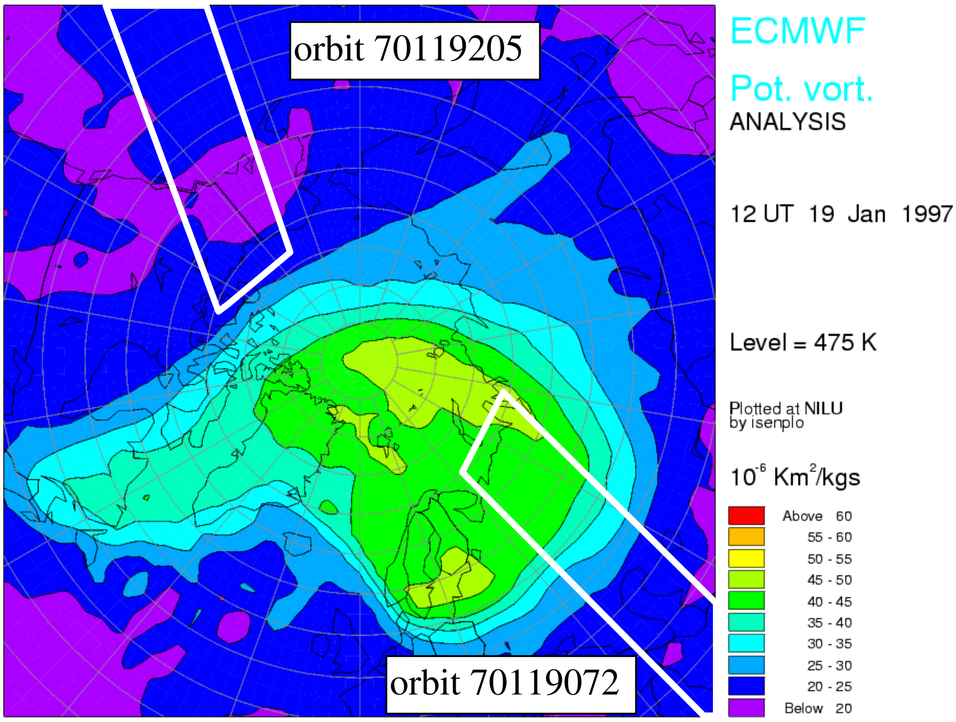


Figure 7.2 Map of the potential vorticity at the level of a potential temperature of 475 K[1] for January, 19, 1997 [ECMWF, 1999]. Also displayed are both orbits (white thick lines) for which the OClO SCDs have been shown in Figure 7.1.

It can be seen that OClO could be measured only inside the polar vortex on that day. For these OClO SCDs a strong increase with increasing SZA can be seen. This is due to an increase of both, the AMF and the OClO concentrations towards higher SZA. Even if the OClO SCDs were converted to VCDs applying the AMF concept (see section 5) the latter dependence would remain. Because of the large uncertainty of the AMF for OClO at large SZA we decided to present OClO SCDs only. For the calculation of OClO VCDs for specific measurements the AMFs calculated in section 5.2.3 can be applied.

Another interesting example of the OClO results for 19.01.1997 is shown in Figure 7.3. For this orbit the edge of the polar vortex as well as the latitude with SZA = 90° are indicated by vertical lines. It can be seen that for SZA above 90° the observed OClO SCD increases strongly. This cannot be expected from the dependence of the AMF from the SZA (see Figure 5.14). Thus it is a clear signal for the increase of the stratospheric OClO concentration with SZA. Enhanced OClO SCDs are only observed inside the polar vortex and they sharply decrease at the vortex edge. This common finding confirms that the vortex edge can be seen as a strong barrier against horizontal transport.

[1] The potential temperature θ is defined as the temperature of an air parcel after it is adiabatically transformed to a reference pressure p_0 of 1000 hPa: $\theta \equiv T \cdot (p_0/p)^{\kappa}$ with T and p the temperature and pressure of the air parcel, respectively. κ is about 0.29 for dry air [Harder, 1999].
For the winter polar atmosphere the level of the potential temperature of 475 K corresponds to an approximate altitude of 19 km (see also Table 7.1).

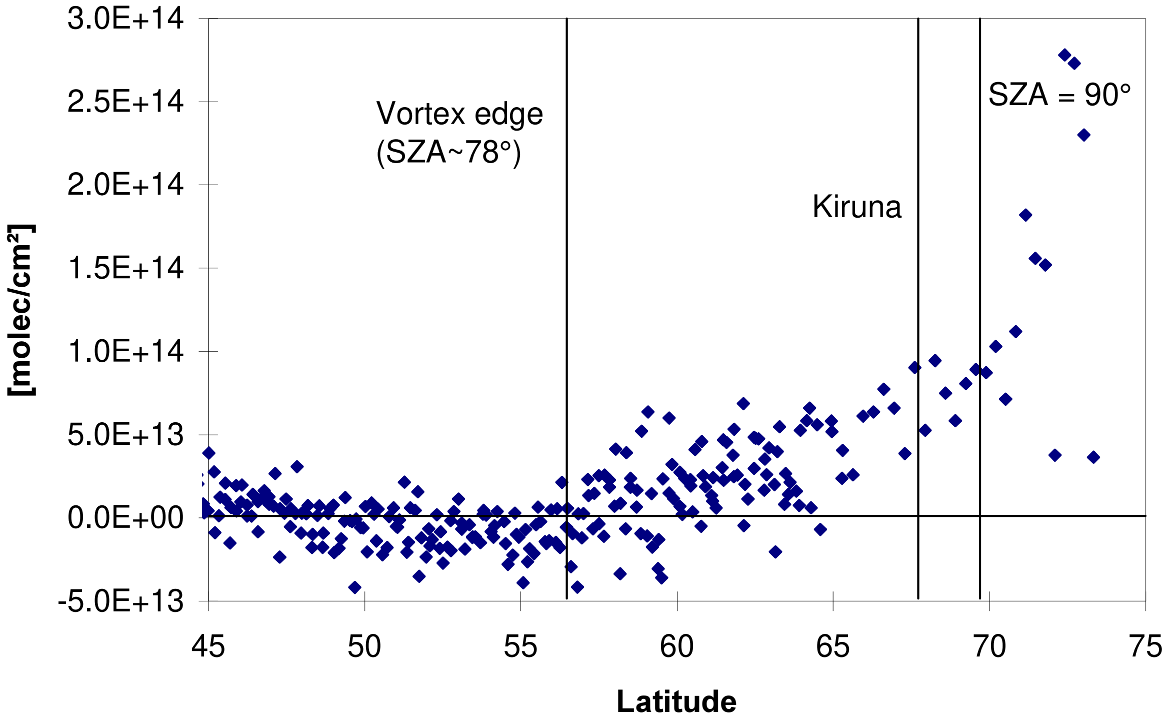


Figure 7.3 OClO SCD for the orbit 70119104 which was located above Scandinavia where the vortex edge reached down to latitudes of about 55°N. North from about this latitude the OClO SCDs increase significantly, enhanced OClO SCDs were observed for SZAs significantly below 80°. This satellite orbit was located also above Kiruna (67.9°N, 21.1°E, see vertical line) where ground based observations of OClO have been performed for the same day (see next section).

7.1.2 Comparison with ground based instruments

The direct comparison of GOME OClO SCDs with the results of simultaneous ground based observations is more difficult than for BrO because for two reasons:

A) The atmospheric OClO absorptions are small compared to BrO, thus the relative uncertainties are large.

B) OClO photolyses rapidly as the sun rises, thus the SZA for the GOME overpass has to be large (very close to 90° or even higher). Such SZA will be only found during winter at high latitudes. For these conditions the diurnal variation of the SZA is only small and the difference between the absorption of the measured spectrum and the Fraunhofer spectrum are only small. In contrast, GOME measures absolute OClO SCDs.

Due to both reasons the comparison of OClO SCDs measured by GOME and ground based instruments is subject to large uncertainties. To derive nearly absolute OClO SCDs also from the ground based measurements a spectrum with relatively high sun from outside the vortex was taken (from April, 17, 1997 for the winter 1996/97 and from April, 6 , 1998 for the winter 1997/98). However, due to the large temporal distances between these Fraunhofer spectra and the measured spectra the errors of the OClO retrieval for ground based measurements can be relatively large (up to 30 %).

For January 19, 1997 the polar vortex was largely displaced from the north pole and covered nearly whole Scandinavia (see Figure 7.2). In particular Kiruna (67.9°N, 21.1°E) was located well inside the vortex and as can be seen from the GOME measurements presented in Figure

7.4 high OClO SCDs were indeed measured above Kiruna. The OClO SCDs over Kiruna measured by GOME are about 7.5±2 $\cdot 10^{13}$ molec/cm² (see Figure 7.3).
The OClO SCD measured from the ground based instrument at Kiruna for the same day are shown in Figure 7.5. It was found that during the GOME overpass the OClO SCD was about 8±2.5 $\cdot 10^{13}$ molec/cm², which is nearly the same as measured by GOME.

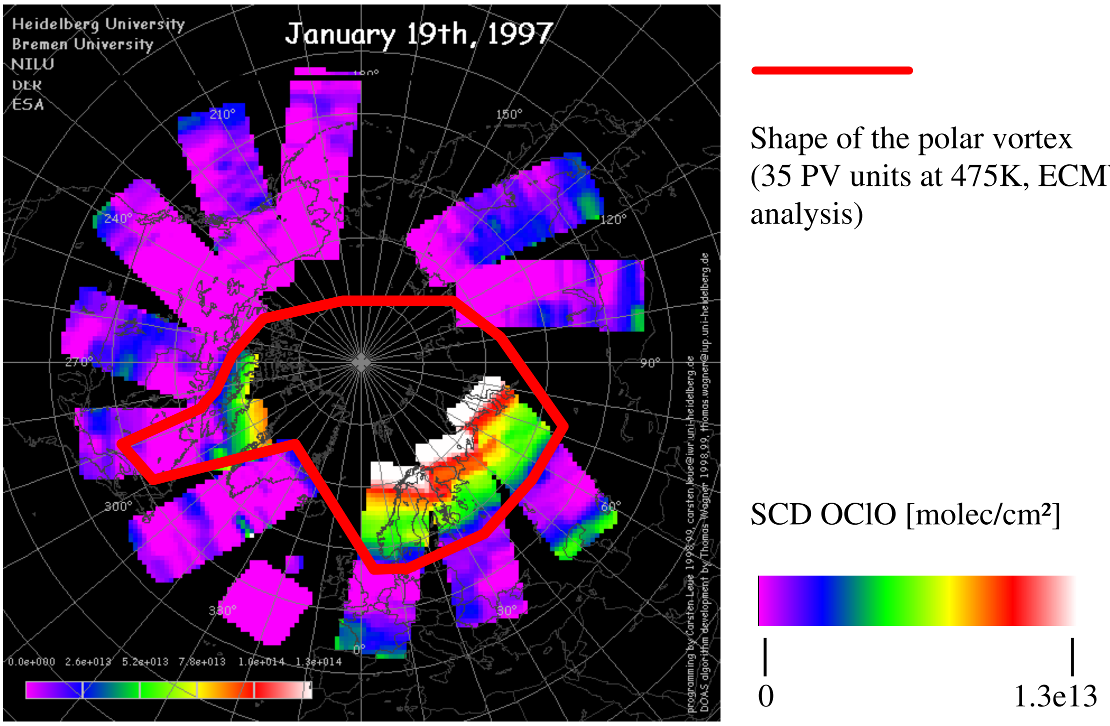


Figure 7.4 OClO SCD on January, 19, 1997 together with the isoline of potential vorticity (see also Figure 7.2). High OClO SCDs were observed only inside the polar vortex.

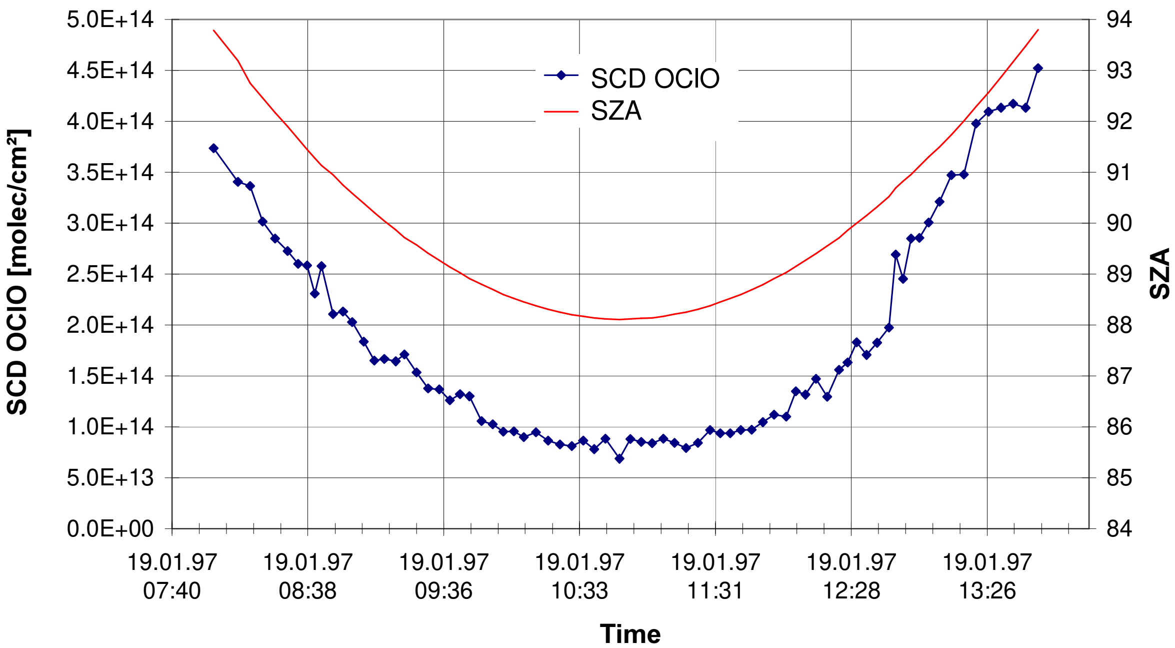
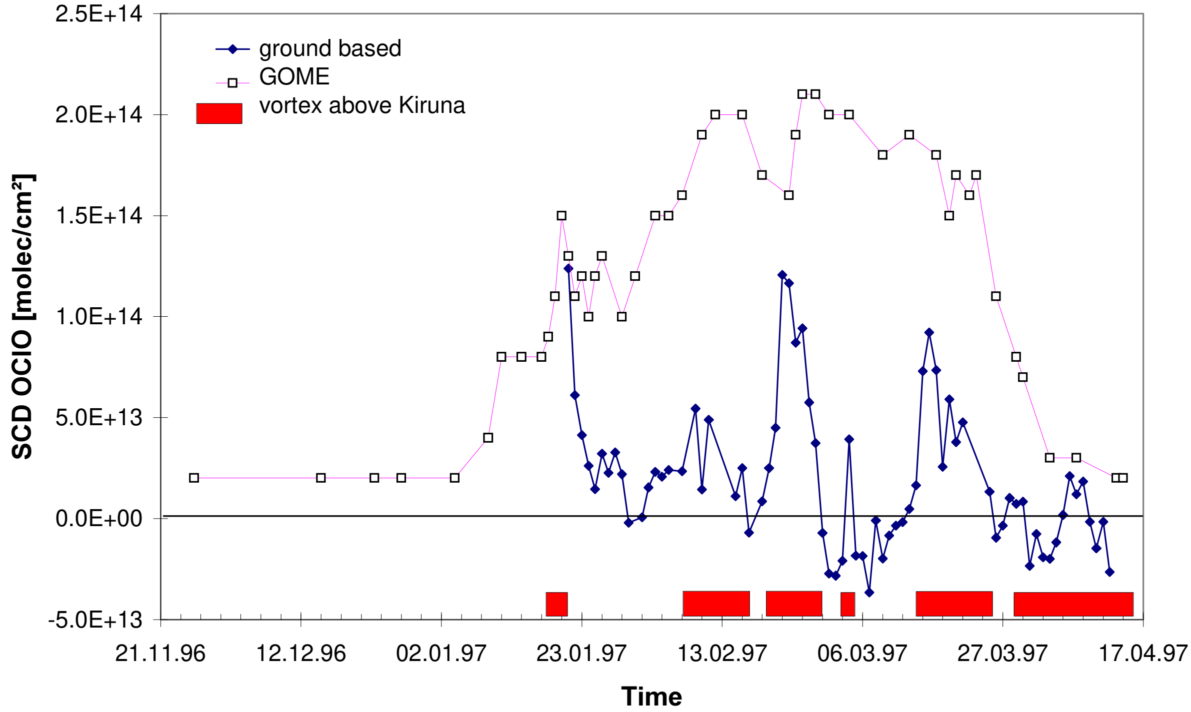


Figure 7.5 OClO SCDs (dots) at Kiruna measured from ground on 19.01. 1997. At local noon (SZA ≈88°, thin line) the OClO SCD is 8±2.5 $\cdot 10^{13}$ molec/cm² which is in good agreement with the GOME OClO observation for the Kiruna overpass of this day (Figure 7.3).

Conditions like for the comparison describe above are relatively rare. In particular for later periods of the winter the SZA for the GOME overpasses above Kiruna decrease rapidly and the OClO SCDs get down below the detection limit.
Thus the data from ground based and satellite measurements were further compared in a different manner: For the GOME measurements the maximum daily OClO SCD measured for a SZA of 90° were determined. Also from the ground based measurements the OClO SCDs for SZA = 90° were selected. For these data sets (except the end of December and the beginning of January) there is no direct spatial and temporal overlap: for GOME the SZA of 90° is reached over areas polewards from Kiruna; for the ground base measurements the SZA of 90° appears before (in the morning) and after (in the evening) the GOME observations at 90° of the same day. However, this selection of data allows to compare both measurements over periods of several months. For GOME the maximum values of the OClO SCD (SZA = 90°) inside the vortex were chosen to monitor the maximum chlorine activation inside the polar vortex as a function of time. It is also important to note that only for the periods in which the polar vortex was located above Kiruna both measurements can be expected to show similar values.
In Figure 7.6 both data sets are presented for the two Arctic winters for which OClO data from ground based measurements at Kiruna are presently available [Wagner et al., 1998f].
For periods during December and January when the SZA for the GOME overpass at Kiruna is close to 90° the OClO SCDs are similar to those measured by GOME when the polar vortex was located above Kiruna (these periods are marked by the horizontal bars at the bottom of the diagrams). As can be expected the OClO SCDs measured from ground are equal or smaller compared to the maximum values for the OClO SCDs inside the polar vortex observed by GOME. In particular for all periods when vortex air was above the ground based instrument enhanced OClO SCDs were measured. However, it is a common interesting feature in both winters that these values decrease systematically towards the end of the winter while the OClO SCDs measured by GOME still remains high.
In particular in 1996/97 from GOME measurements it was found that the chlorine activation continues for a period of several months. Also in the much warmer winter 1997/98 the GOME observations show enhanced OClO SCDs at the end of winter when the ground based OClO data seem to indicate already a recovery into the reservoir species.
These findings indicate one of the main advantages of GOME: The measurements can monitor the temporal and spatial evolution of atmospheric trace gases. For example, in the winter 1997/98 GOME data clearly indicate that the chlorine activation of the stratosphere lasts about one months longer than observed from the ground based instrument at Kiruna.



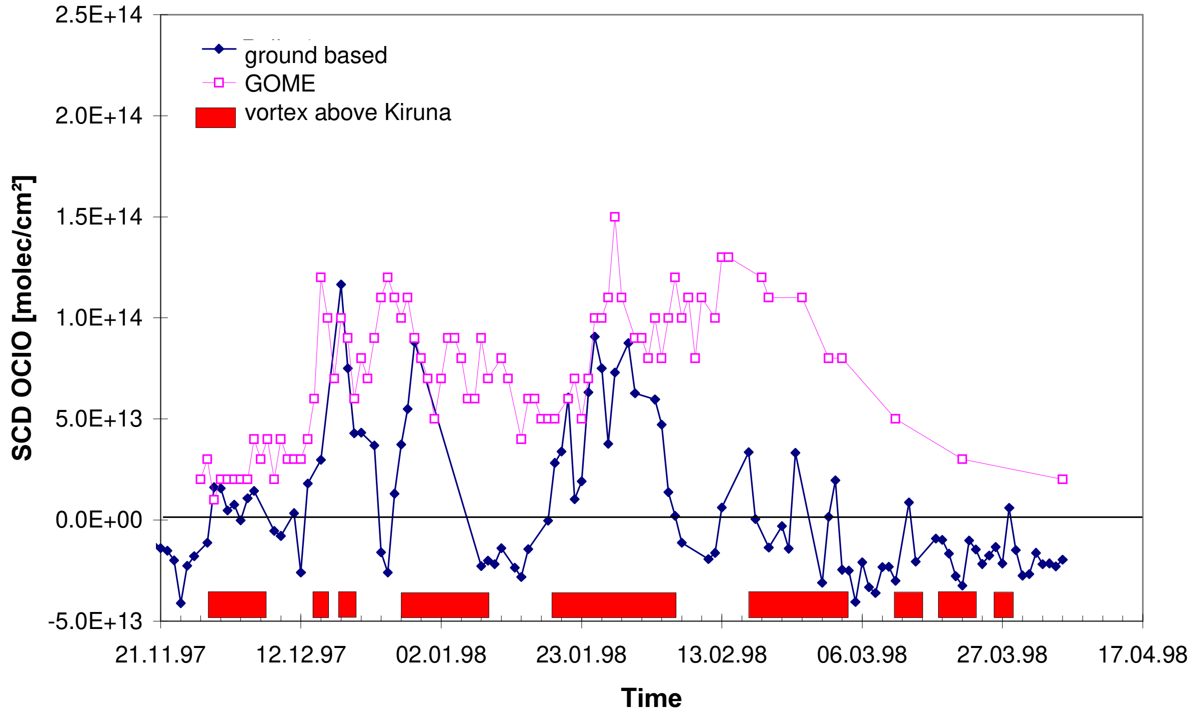


Figure 7.6 Comparison of OClO SCDs at 90° measured from ground (at Kiruna) and from satellite. For the GOME measurements the maximum daily OClO SCDs for a SZA of 90° were chosen. Also for the ground based measurements the OClO SCDs for SZA = 90° were selected. It should be noted that (except in mid winter) no direct spatial and temporal overlap of both data sets exist. However, it can be seen that for periods with the vortex above Kiruna the OClO SCDs from the ground based instrument are similar or smaller compared to the GOME data. At the end of winter the GOME data indicate a longer duration of the chlorine activation than the ground based measurements.

7.1.3 Time series of GOME OClO observations in the northern hemisphere

At present OClO GOME data of all Arctic and Antarctic winters since the launch of GOME have been analysed. This allows to compare the temporal evolution of the chlorine activation for different winters in the northern hemisphere. While in the Antarctic the time series of the stratospheric temperatures are very similar for different years (see Figure 2.15) in the northern hemisphere a very large year to year variation is found. The four winters since 1995 cover nearly the full range of the temporal evolution observed in the northern hemisphere so far: The winters 1995/96 and 1996/97 belong to the coldest winters and in particular to those with the longest continuous periods of cold temperatures. In 1997/98 the minimum stratospheric temperatures fall only sporadically below the threshold temperature for the formation of PSCs. Finally the winter 1998/99 was one of the warmest observed so far and the formation threshold for PSCs was reached only seldom.
As a common feature a large temporal variability for the start and the end of the possibility of the PSC formation was observed during these four years.
Figure 7.7 presents time series of daily maximum OClO SCDs (at 90° SZA) measured by GOME as well as the daily minimum stratospheric temperatures at an isosurface of 475 K potential temperature [ECMWF, 1999] (As will be demonstrated in the next section the highest (anti-) correlation between OClO and temperature was found for the 475 K level).

For all four winters chlorine activation was indicated by enhanced OClO SCDs. However, the magnitude of the OClO SCDs and the duration of the periods of enhanced values varies markedly. While there seems to be a general anticorrelation between the OClO and temperature data even for temperatures above 195 K, a pronounced chlorine activation could be observed just below 195 K.
One exception, however, can be found in the winter 1997/98 when during the beginning and mid of February the OClO SCD increase while the temperatures are slightly above 196 K. This indicates that e.g. there might exist local temperature minima lower than the synoptic temperatures used here. Another possible reason was that at other altitudes the temperatures are below the formation threshold for PSCs, but it was found no clear indication for this assumption from the temperature maps of other altitudes.
In 1995/96 and 1996/97 continuously enhanced OClO SCDs were observed over periods of several months corresponding to simultaneous low stratospheric temperatures. In 1995/96 the chlorine activation starts and ends about one month earlier than in 1996/97 in excellent agreement with the evolution of the stratospheric temperatures. It is interesting to note that in 1996/97 the chlorine activation persisted until the end of March which is of particular importance for the photochemical ozone destruction because towards the summer the availability of solar radiation increases strongly. As can be seen in section 7.1.5 the chlorine activation in the Arctic winter 1996/97 lasted nearly as long as it usually does in the Antarctic winter. For both winters enhanced OClO SCDs have been observed for about two to three weeks after the minimum temperatures have increased above 195 K.
The following two winters were significantly warmer than the ones before. Thus the OClO SCDs were lower and appeared more sporadically than in the winters of 1995/96 and 1996/97. Nevertheless, also in 1997/98 chlorine activation took place until early March.
The stratospheric temperatures in 1998/99 were among the highest observed so far. Only at the end of November and at the beginning of February temperatures dropped down below 195 K and a weak enhancement of the OClO SCDs was observed. During this winter a stratospheric cooling already appeared at the end of November leading to a very early chlorine activation during this winter.

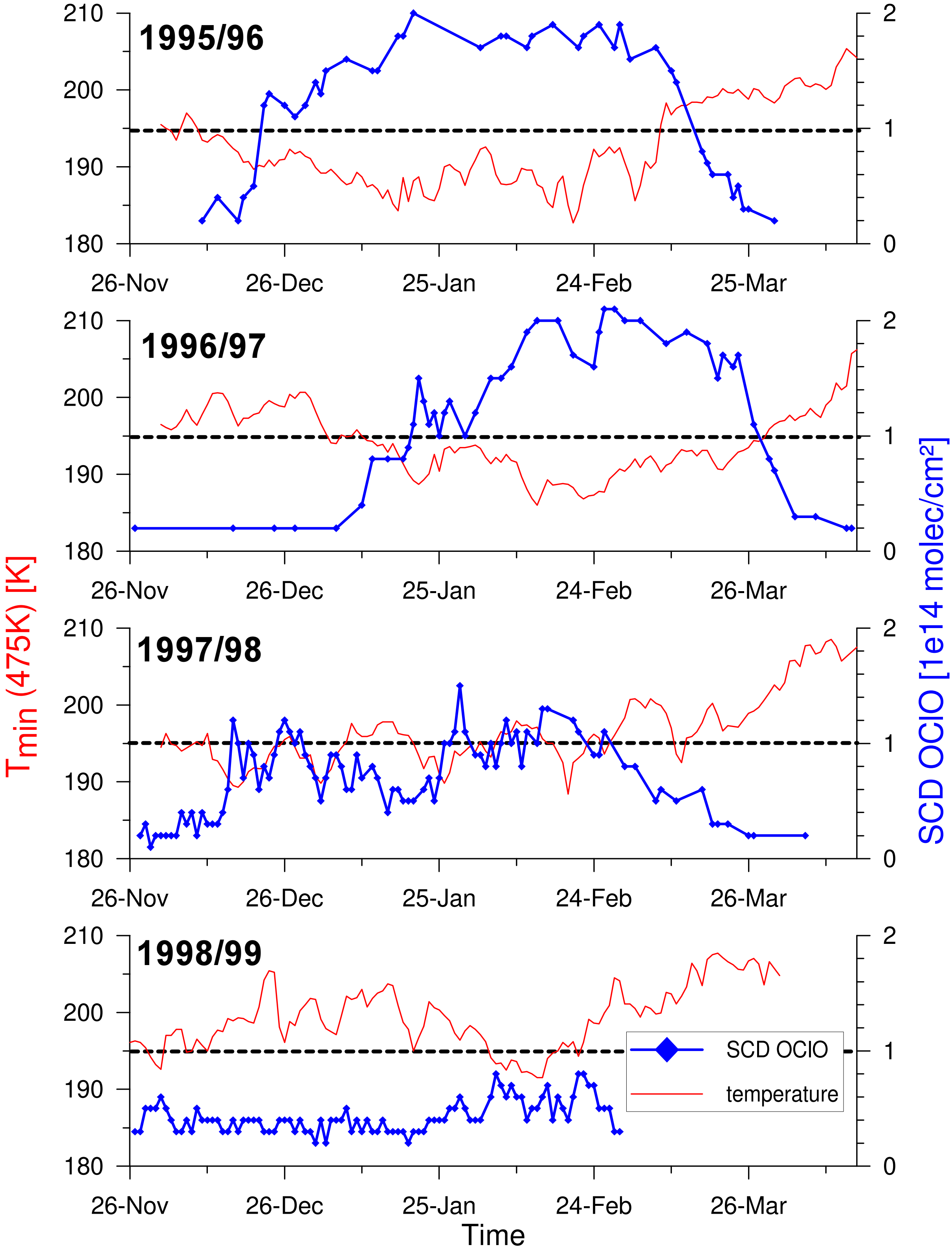


Figure 7.7 Time series of the daily maximum OClO SCDs (at a SZA of 90°) observed by GOME and the minimum stratospheric temperatures at the 475 K level (from ECMWF data) for the four Arctic winters after the launch in 1995. Because of the huge amount of data OClO could not be analysed for all days so far. Thus the true variability is expected to be larger. Most effort of the OClO analysis was spent to periods with large temperature variations. The formation threshold for PSCs is indicated by the dashed line.

Figure 7.8 shows OClO maps for days when maximum SCDs for the different Arctic winters were observed. According to the above findings (Figure 7.7) the OClO SCDs and the areas are larger in the two first winters compared to the two following ones. It is interesting to note that even in 1998/98 enhanced OClO VCDs could be observed over a large area although stratospheric temperatures were particularly high.

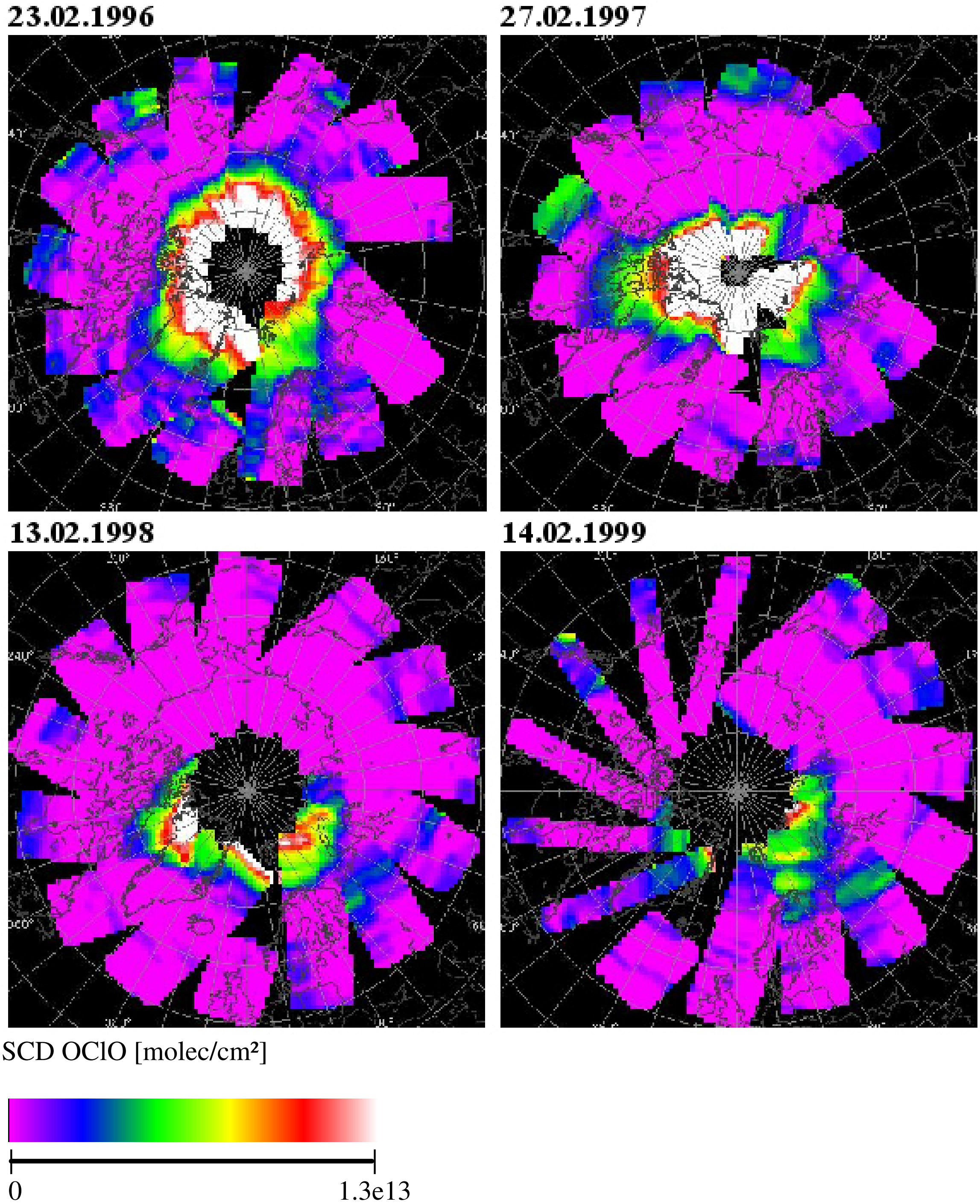


Figure 7.8 GOME OClO maps for days of the maximum SCDs observed in the northern hemisphere for different years. The magnitude of the OClO SCDs and the area with enhanced values are significantly larger in the two first winters compared to the two following ones.

7.1.4 Temperature dependence of Chlorine activation in the Arctic

It was shown in section 7.1.3 that the formation of OClO is sensitive to the temperature threshold of about 195 K at the altitude level at 475 K potential temperature (Figure 7.7). To study this temperature dependence in more detail the daily maximum OClO SCDs of all Arctic winters are plotted as a function of the minimum temperatures at different potential temperature levels (Figure 7.9) corresponding to different altitudes (see Table 7.1).

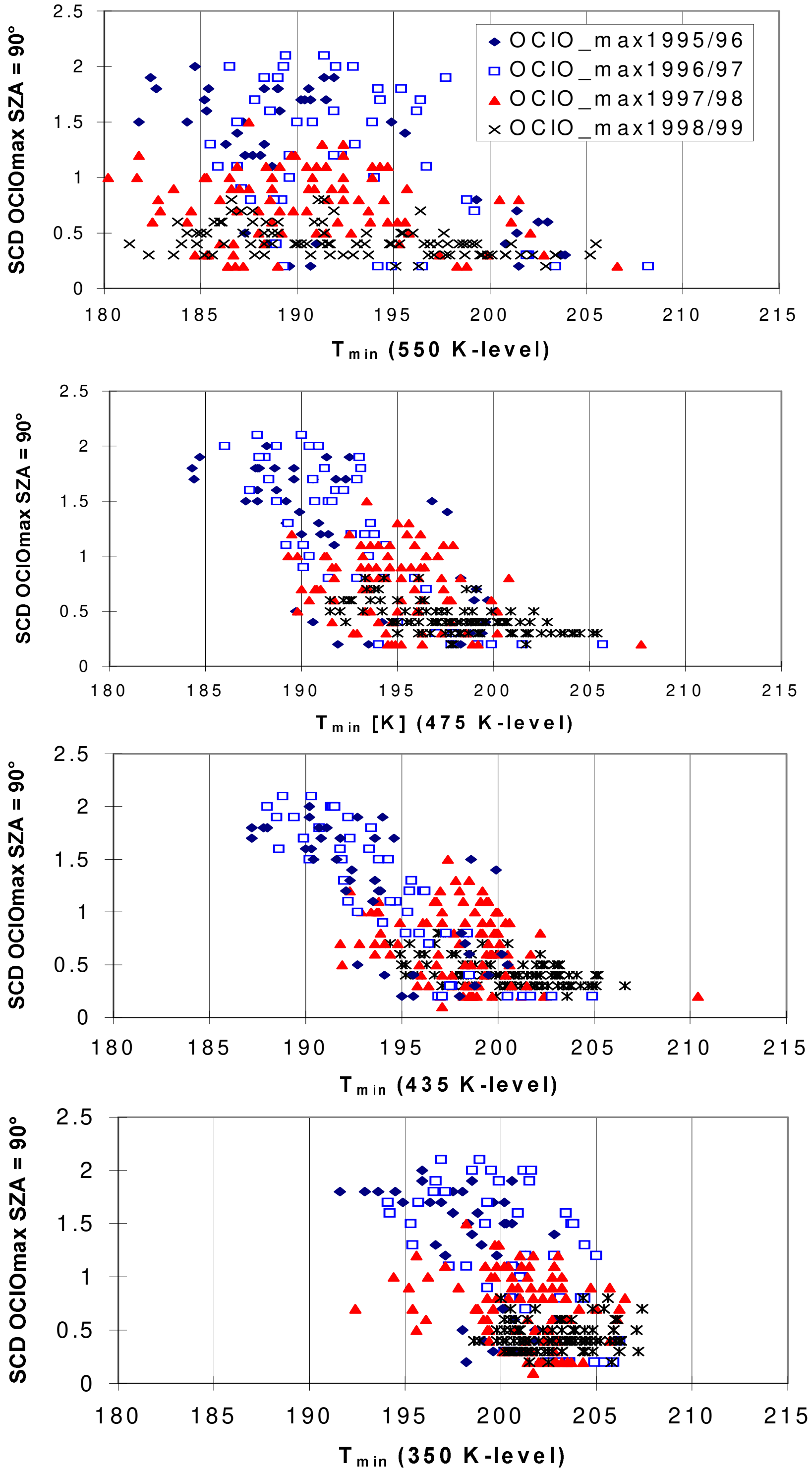


Figure 7.9 Scatter plots of the maximum OClO SCDs and the minimum temperature for different altitudes. Surprisingly, in particular for the 550 K level no correlation was found.

potential temperature [K]	approximate altitude [km]
350	12
400	16
475	19
550	22

Table 7.1 Approximate altitudes according to different potential temperatures typical for the Arctic winter atmosphere [Harder, 1999].

The best (anti-) correlation was found for the levels of a potential temperature of 475 K, and 400 K. In contrast, there is only a weak correlation with the minimum temperatures at the 350 K level and almost no correlation at the 550 K level. This is a common feature found in all four winters.
We conclude that the chlorine activation takes place mainly at altitudes related to a potential temperature of 475 K and below.
To investigate this temperature dependence in more detail we removed all OClO data for the periods at the end of the winter when the already decreasing OClO SCDs are still high while the temperatures have already significantly increased. During these periods enhanced OClO SCDs are expected to belong to retarded conversion into the reservoir species rather than to a still ongoing chlorine activation. The resulting scatter plot for 475 K is shown in Figure 7.10.
It was found that many enhanced OClO SCDs are observed at minimum temperatures between 195 K and 198 K. However, only below 195 K a strong enhancement could be found. For temperatures below 190 K the OClO SCDs show no further increase. This saturation effect might indicate an upper limit of chlorine activation in the Antarctic winter.
It should be noted that during polar night GOME cannot observe the center of the polar vortex, thus underestimating the actual maximum OClO SCDs. Indeed the low OClO SCDs observed at temperatures below 195 K all belong to such days of the winters 1995/96, 1997/98 and 1998/99.

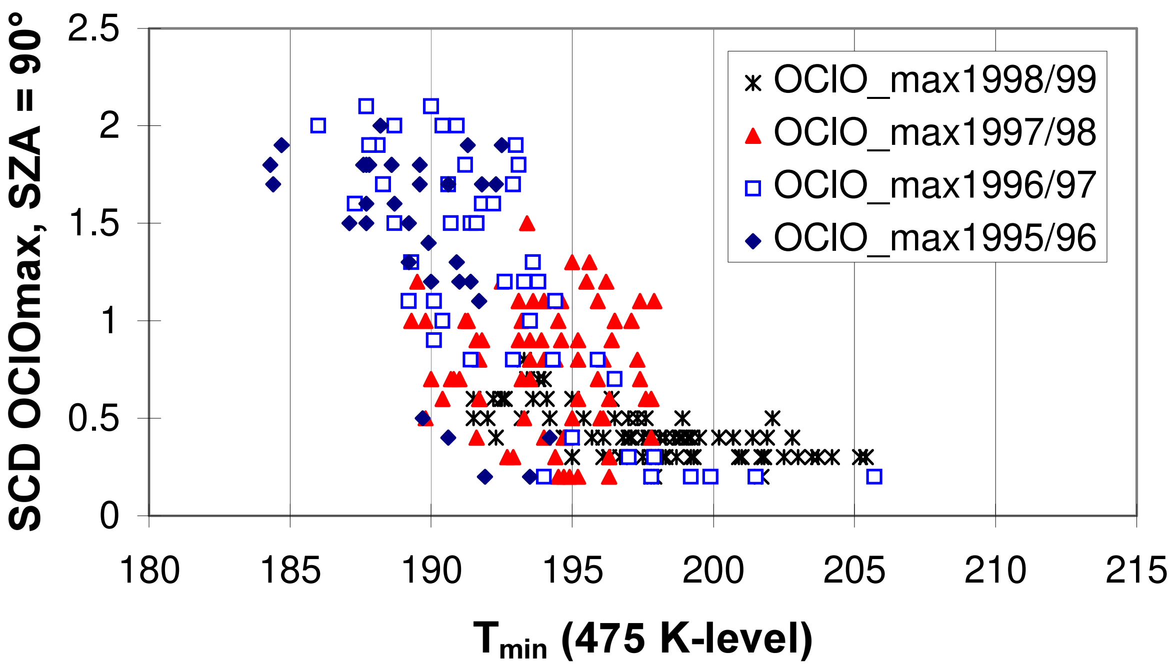


Figure 7.10 Scatter plot of the maximum OClO SCDs and the minimum temperature for the 475 K potential temperature level. Here all OClO data were removed for the periods at the end of the winters (see text).

7.1.5 Comparison between both hemispheres

In contrast to the northern hemisphere the temporal evolution of the antarctic stratospheric temperatures is very uniform for different years (see also Figure 2.15). Accordingly, the time series for the daily maximum OClO SCDs also show a very similar development (Figure 7.11).

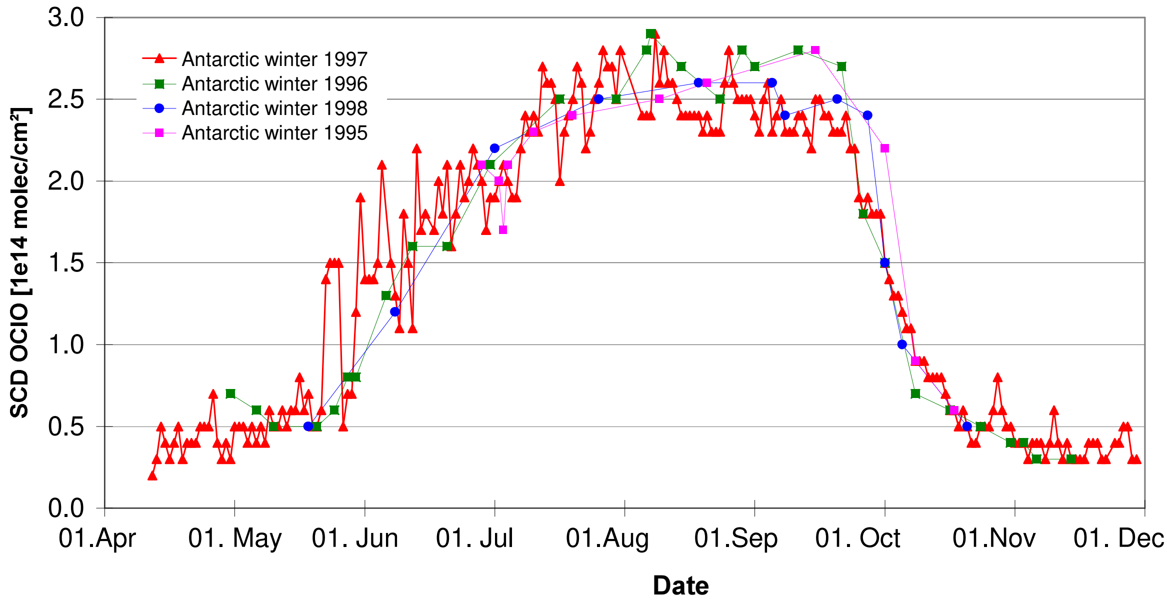


Figure 7.11 Time series for the daily maximum OClO SCDs observed during Antarctic winter for the years 1995 to 1998. The OClO SCDs are very similar for the different years.

In all observed winters (1995 to 1998) significant chlorine activation starts at the end of May and the maximum OClO SCDs remain high continuously during the whole winter. At the end of September the OClO SCDs quickly decrease and the chlorine activation ends around the end of October. In total a strong chlorine activation in the Antarctic winter/spring occurs typically for a period of about 4 months.

It should be noted that due to the huge amount of data it was not possible to analyse all spectra for the respective winters. Only the data for the winter 1997 have been analysed on a daily basis. Thus, there might be possible variations of the data for the other years which are not covered with the presently existing data set. However, the overall agreement of the OClO SCDs for all observed winters indicates that this is not very probable.

In Figure 7.12 OClO time series for both hemispheres are compared. Several general differences between both hemispheres are obvious:

A) The temporal variability in the northern hemisphere is much stronger compared to the southern hemisphere.

B) The periods of chlorine activation in general start later and end earlier in the northern hemisphere compared to Antarctica. In consequence the total duration of the chlorine activation during the Arctic winter is significantly shorter than in the Antarctic winter.

C) The maximum values in the northern hemisphere are about 70% of those in the southern hemisphere indicating a weaker chlorine activation there.

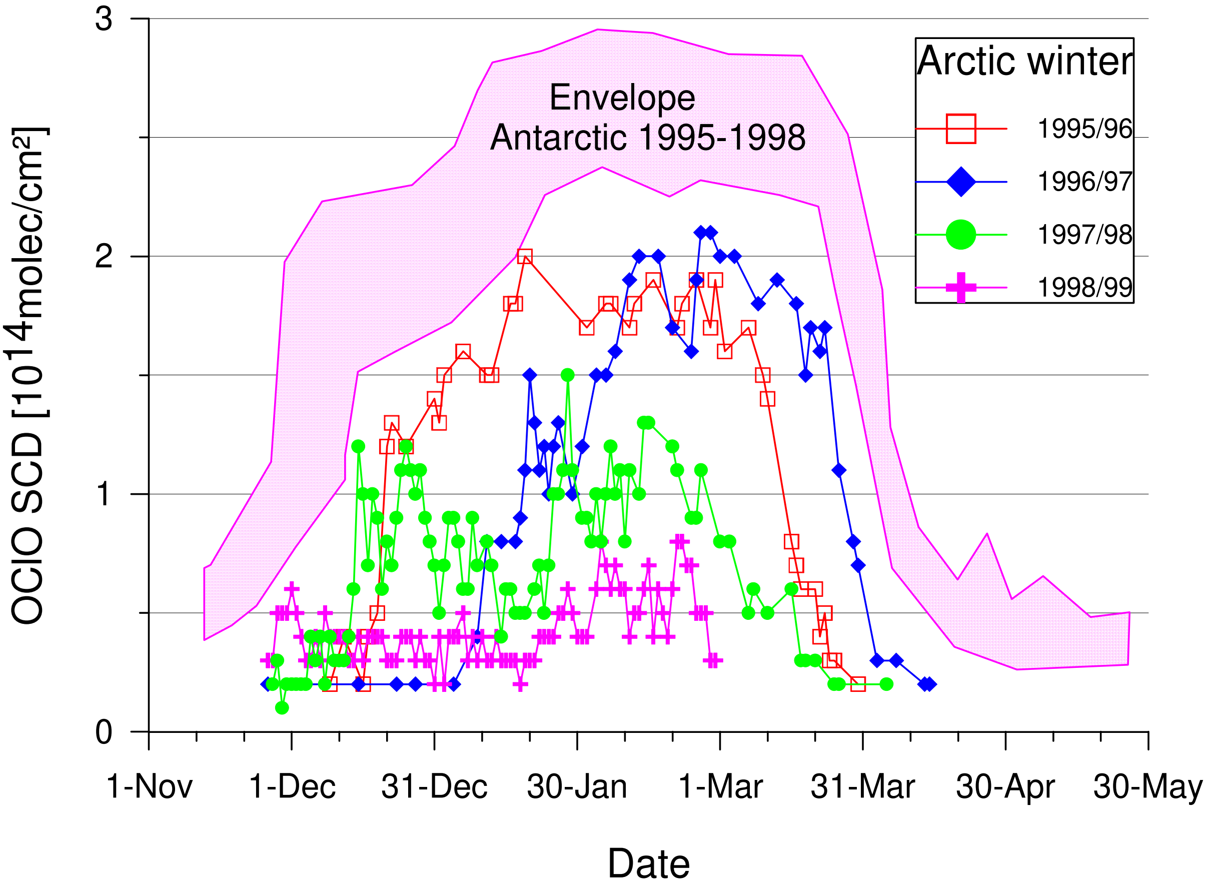


Figure 7.12 Time series of the daily maximum OClO SCDs for both hemispheres in the winters 1995 to 1998. The OClO SCDs measured in the Antarctic winters (Figure 7.11) are represented by an envelope and shifted by 6 months.

7.1.6 OClO outside the polar vortices?

For several cases slightly enhanced OClO SCDs have been observed outside the polar vortex. However, most of them are not significant. The detection limit of OClO at present state (≈22 to $35 \cdot 10^{12}$ molec/cm, depending on the SZA) is still too high to measure low amounts of OClO as reported e.g. by Erle et al. [1999]. Such studies will hopefully be possible in the future.

Figure 7.13 presents OClO SCDs measured on February, 14, 1999 when filaments of the (weak) vortex are located above Europe. Over this region also enhanced OClO SCDs are found (Figure 7.13 right).

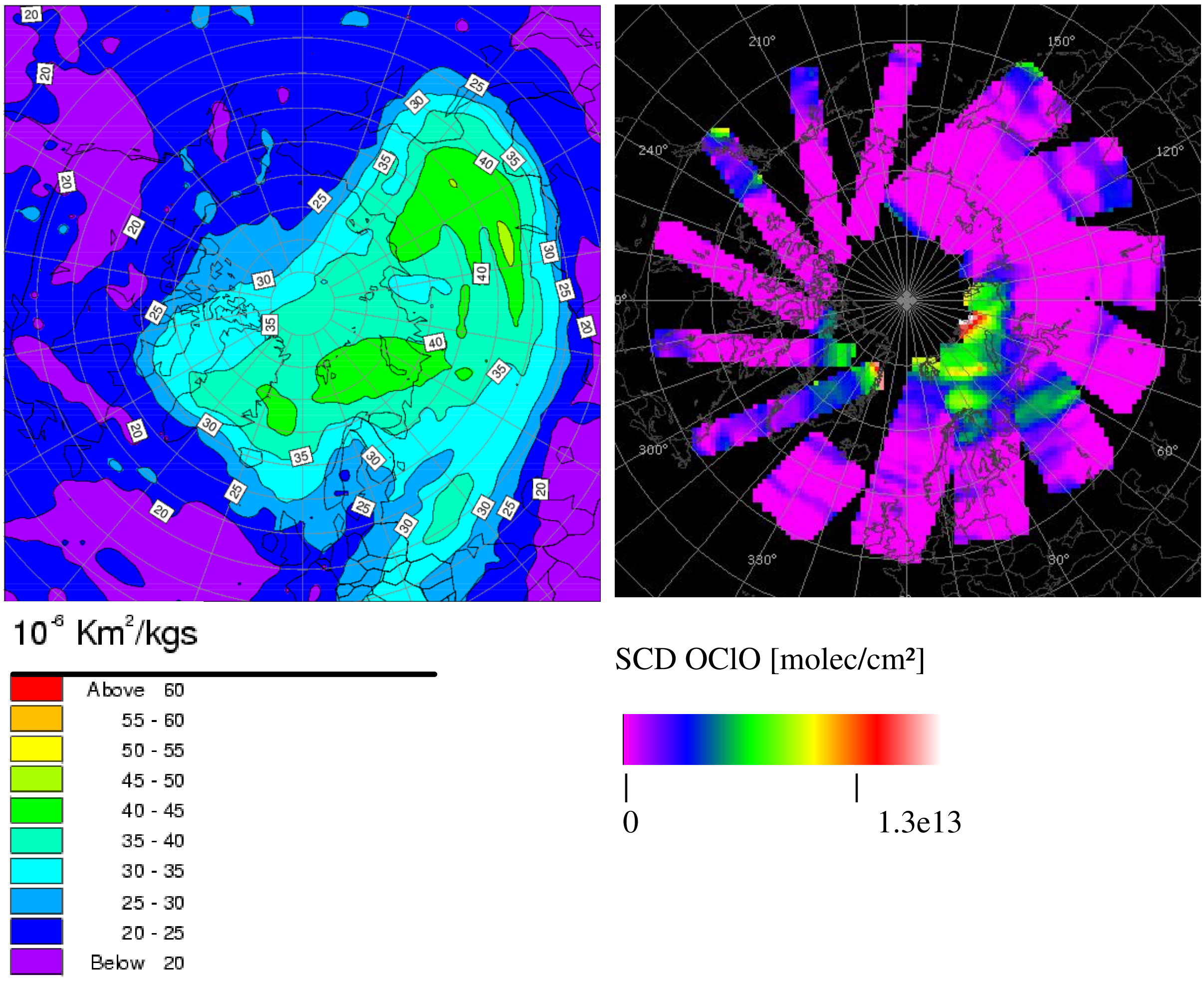


Figure 7.13 Map of the potential vorticity at the 475 K level (left) and the maximum OClO SCD (right).

7.1.7 Time constant of chlorine activation, mixing inside the vortex

From GOME data it is possible to derive information on the efficiency of the mixing processes inside the polar vortex as well as on the speed of chlorine activation.
In Figure 7.14 some examples for the time series of the daily maximum OClO SCDs for both hemispheres are presented. During these periods the measured OClO SCDs increase very fast within one or two days from ‘background values’ to about 1.2 to $1.5 \cdot 10^{14}$ molec/cm².
One of these periods of rapid chlorine activation is presented in more detail in Figure 7.15. The temperature of the stratosphere decreased below 195 K on December, 10 and even lower during the following days. For the same period the OClO SCDs increased significantly. It is interesting to note that the complete area inside the polar vortex which can be observed by GOME shows high OClO SCDs. This indicates that the air of the polar vortex is well mixed within a few days.

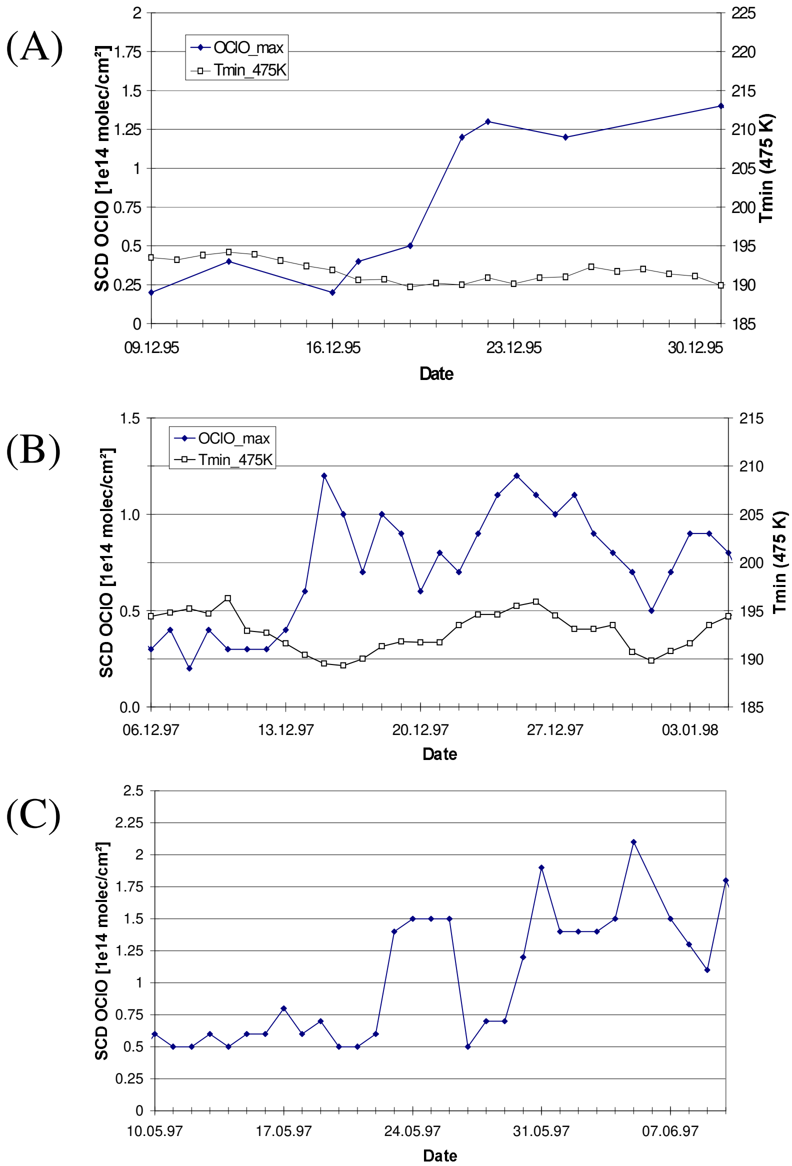


Figure 7.14 Examples of periods when very rapid chlorine activation was observed in both hemispheres (A: Arctic winter 1995/96, B: Arctic winter 1996/97, C: Antarctic winter 1997). For the northern hemisphere also the minimum temperatures are shown. OClO SCDs increase form 'background values' to about 1.2 to 1.5 $\cdot 10^{14}$ molec/cm² within one to two days. The example of December 1997 (B) is presented in more detail in Figure 7.15.

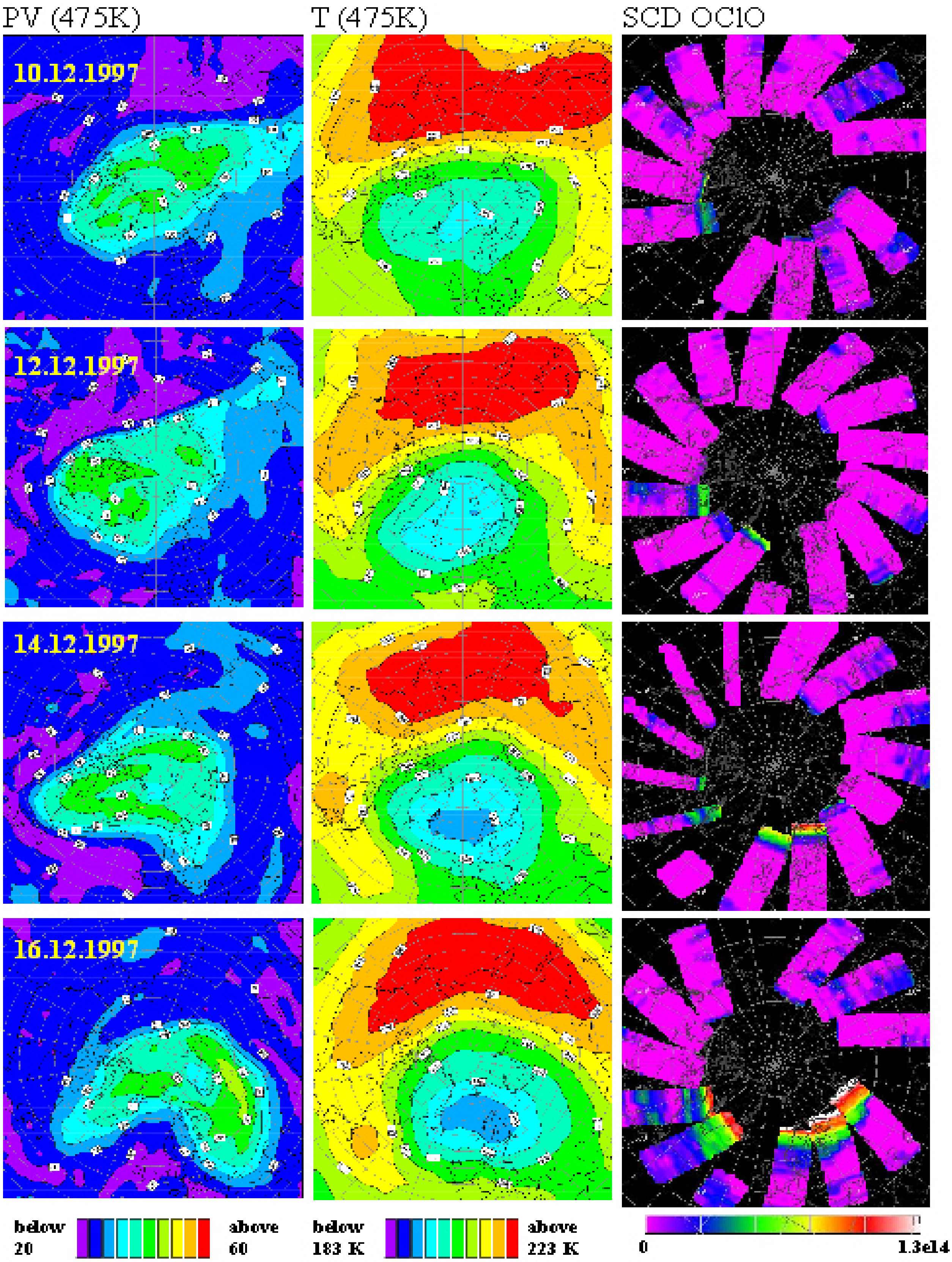


Figure 7.15 Example of rapid chlorine activation. Displayed are maps of the potential vorticity and the temperature at the 475 K level as well as the OClO SCD for December, 10 to 16. On December, 10 the temperatures drop below 195 K in a small region inside the polar vortex, the respective areas become significantly larger during the following days indicating a strong cooling of the stratosphere. During the same period the OClO SCDs inside the polar vortex increase rapidly.

7.2 OClO maps for THESEO

The knowledge of the actual stratospheric chlorine activation is a very useful information for the timing of field activities like balloon soundings. This was of interest in particular during the THESEO campaign (http://salines.aerov.jussieu.fr/experience/THESEO/) in January and February 1999 when several balloons were launched at ESRANGE near Kiruna.
To support the planning of the THESEO field activities within the activities of the GODIVA project (Tanzi and Goede, [1999], see also: http://www.sron.nl/divisions/eos/godiva) the GOME OClO algorithm developed in this PhD thesis was implemented in an automatic DOAS routine [Leue, 1999] and provided to the Norwegian Institute for Air Research (NILU) [Braathen, 1996]. There daily maps of OClO SCDs were processed in near real time and made available via the NILU web page (http://www.nilu.no/projects/nadir/index.html). From January to April 1999 the satellite data for most of the daily orbits (at the Kiruna receiving station the GOME data for 10 of 14 daily orbits are received) were transmitted to NILU. Since the beginning of February OClO maps were available via the NILU web-page about only one day after the measurement.

7.3 OClO in the troposphere?

In this section an upper limit of the OClO concentrations during an event of enhanced BrO concentrations in the polar boundary layer is determined. BrO and Cl have been detected in the boundary layer [Tuckermann et al., 1997]. Thus OClO can be expected to be formed by the reaction of BrO with ClO. In addition, from the measurement of OClO and BrO it might be possible to estimate the concentration of ClO.
In the stratosphere during ozone hole conditions typical BrO and ClO concentrations are about $2\cdot10^7$ molec/cm³ and $2\cdot10^9$ molec/cm³, respectively [Pundt et al., 1999; Harder et al., 1998; Waters et al., 1993] (at about 18 km). To the contrary, during events of enhanced BrO concentrations BrO is the more abundant species being present at concentrations up to about to $1\cdot10^9$ molec/cm³ [Tuckermann et al., 1997] (see also section 6.3.3).
Applying the above numbers for the stratosphere [BrO] · [ClO] is about $4\cdot10^{16}$ molec²/cm^6, for the troposphere $2.5\cdot10^{17}$ molec²/cm^6, nearly an order of magnitude higher than for the stratosphere. Thus substantial amounts of OClO might also have formed during events of enhanced BrO concentrations in the boundary layer.
Figure 7.16 shows BrO and OClO data for an GOME orbit where enhanced BrO concentrations in the boundary layer have been observed (60915214, see also Figure 6.6). From the enhancement the BrO concentrations were estimated to about $1\cdot10^9$ molec/cm³ (see Table 6.2).
From the uncertainty of the simultaneous OClO observations ($3\cdot10^{13}$ molec/cm²) we can estimate an upper limit for the OClO concentrations in the boundary layer. Assuming a layer height of about 1 km (as for the BrO measurements, see also section 6.3.3) we derive an upper limit for the OClO concentration of about $1\cdot10^8$ molec/cm³ corresponding to an OClO mixing ratio of about 3.5 ppt.
It should be noted that at about 75° SZA OClO is expected to be photolysed rapidly in the stratosphere [Sessler et al., 1995]. This relatively small SZA was chosen to separate possible tropospheric OClO absorptions from those in the stratosphere which increase significantly at higher SZA (as seen in Figure 7.16). The photolysis frequency in the boundary can be expected to be significantly lower than in the stratosphere [Lehrer, 1999].

The upper limit for the OClO mixing ratio in the boundary layer of 3.5 ppt can be used as input (together with the BrO data) to modelling studies in order to derive an upper limit for the ClO mixing ratios.
A rough estimate for ClO concentrations during the event of enhanced BrO concentrations described above can be derived assuming a steady state between formation and destruction of OClO:

$$\frac{d}{dt}[OClO] = [BrO]\cdot[ClO]\cdot k - [OClO]\cdot J = 0 \qquad (7.1)$$

It follows:

$$[ClO] = \frac{[OClO]\cdot J}{[BrO]\cdot k} \qquad (7.2)$$

The photolysis rate for OClO in the boundary layer is about $3.6 \cdot 10^{-2}\ s^{-1}$ [Lehrer, 1999], about one order of magnitude lower than in the stratosphere [Sessler et al., 1995]. The value for k is taken from De More et al. [1994] for a temperature of 250 K to about $8.9 \cdot 10^{-12}$ $cm^3 molec^{-1} s^{-1}$. With the above concentrations for BrO and OClO we derive an upper limit for the ClO concentration during the event of enhanced boundary layer BrO concentrations of about $4 \cdot 10^{-8}$molec/cm³.

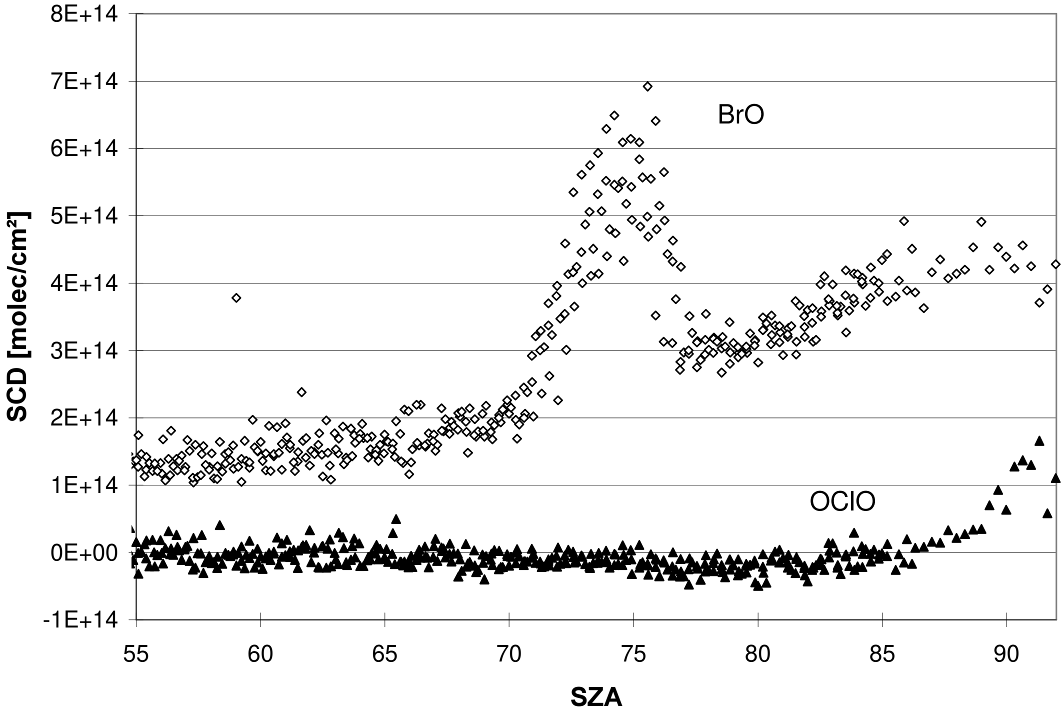


Figure 7.16 BrO and OClO SCDs for an orbit with enhanced boundary layer BrO concentrations (60915214, see also Figure 6.6). The simultaneously measured OClO values are not enhanced indicating small OClO mixing ratios in the troposphere (see text).

7.4 Summary of the GOME OClO measurements

GOME spectra were analysed with respect to OClO absorptions for the period from 1995 to 1999 in both hemispheres. Thus it was in particular possible to study the spatial and temporal evolution of the stratospheric chlorine activation during polar winter/spring. From our measurements we draw the following conclusions:

- GOME OClO observations are in good agreement with measurements made from ground. In contrast to ground based measurements GOME can observe large areas including large parts of the polar vortex. Thus GOME observations are almost independent from the vortex location.

- Large differences in the OClO SCDs were found for several Arctic winters. In 1995/96 and 1996/97 enhanced OClO SCDs were continuously observed during several months; in the two following winters enhanced OClO SCDs occurred only sporadically and were smaller than in the two first winters.

- In the southern hemisphere the time series of the OClO SCDs are very similar for all winters. The duration of the chlorine activation was found to be at least 1 month longer than in the northern hemisphere. The maximum OClO SCDs observed in the Arctic are about 70 % of those observed in the Antarctic.

- For several cases a substantial stratospheric chlorine activation (from ‘background values’ to about 50% of the maximum OClO SCDs) occurred within one or two days. In one example enhanced OClO SCDs were found within the entire polar vortex about 6 days after the chlorine activation had started.

- In several cases enhanced OClO SCDs were observed at air masses belonging to filaments of the polar vortex.

- The OClO SCDs were found to be anticorrelated to the minimum temperatures at the potential temperature levels of 475 to 400 K. In contrast, for the 550 K level no correlation was found. This seems to indicate that most of the chlorine activation occurs below the 550 K level (about 22 km). However, it should be noted that the stratospheric BrO concentration strongly decreases with height, possibly limiting the formation of OClO at higher altitudes.

- The temperature dependence of the observed OClO SCDs was investigated for the 475 K level in the Arctic stratosphere. Many enhanced OClO SCDs were observed at minimum temperatures between 195 K and 198 K. However, only below 195 K a strong enhancement could be found. For temperatures below 190 K the OClO SCDs show no more increase. This saturation effect might indicate an upper limit of chlorine activation in the Antarctic winter.

- An upper limit for the OClO mixing ratio in the boundary layer during an event of enhanced BrO concentration of about 3.5 ppt was determined corresponding to an upper limit of the ClO mixing ratio of about 14 ppt.