Chapter 6

Results of the BrO measurements

In this section the results of the GOME BrO measurements are presented. The first section gives an overview of the latitudinal variation of the total BrO column densities. In section 6.2 the GOME data are compared to the stratospheric BrO VCD, section 6.3 and 6.4 present GOME observations of BrO in the boundary layer and the free troposphere, respectively.

6.1 Latitudinal and seasonal variability of the BrO VCD measured by GOME

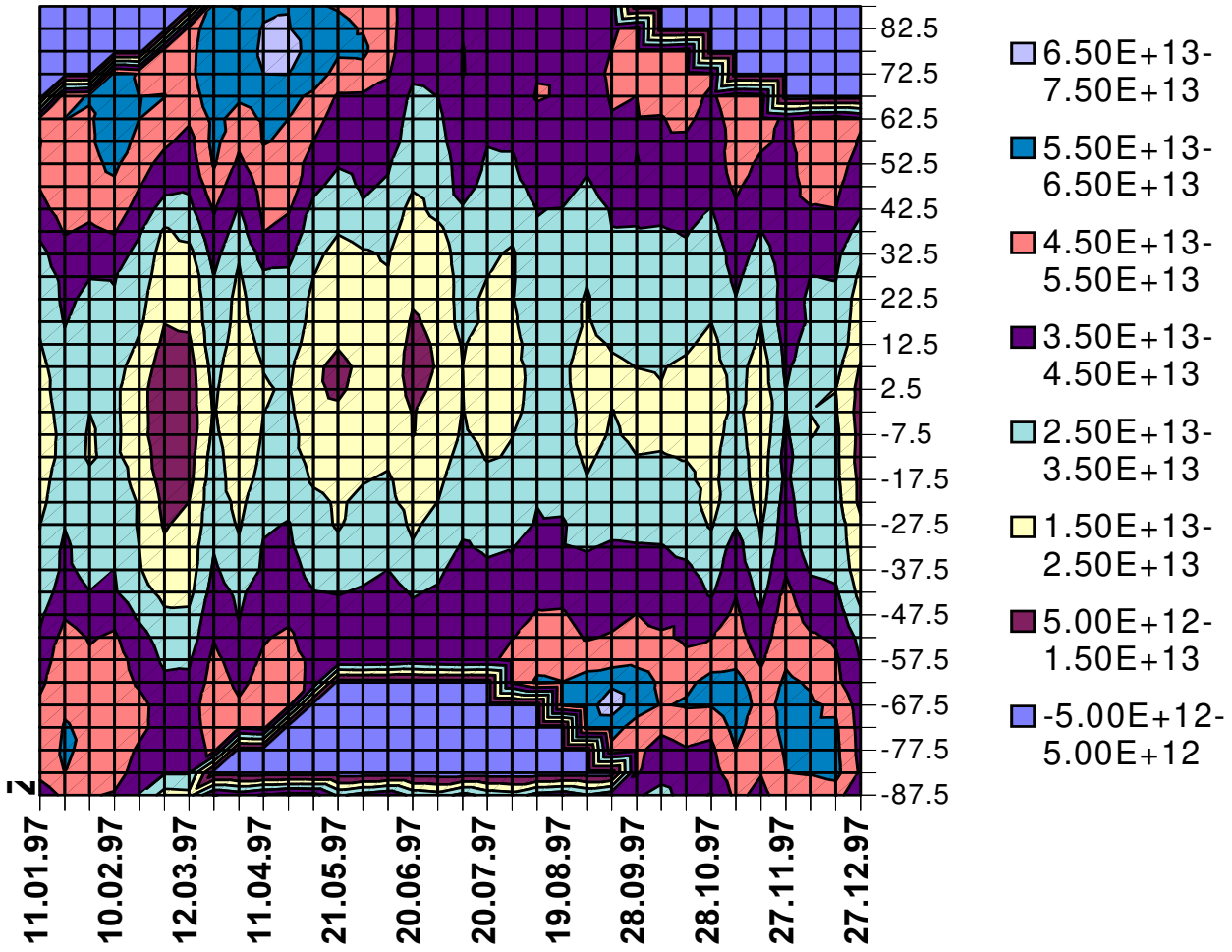


Figure 6.1 Seasonal and temporal variation of the BrO VCD measured by GOME. Displayed are global 30-day averages with a 10-day distance. The values are averaged also for latitude bands of 5 degrees. The blue areas indicate regions of the polar night where the SZA is above 90°. For such conditions the uncertainties due to the AMF are much stronger than for smaller values (see section 5.2.1) Thus we excluded these data.

To investigate the global behaviour of the atmospheric BrO measured by GOME the BrO vertical column densities are calculated. Here we used a 'standard AMF' calculated for a tropopause height

of about 10 km (see section 5.2.1) most appropriate for mid and high latitudes. Although at mid latitudes and in the Tropics the atmospheric height profiles can be located significantly higher, the associated errors of the AMF can be expected to be relatively small (< 7%, see section 5.2.1), since for these latitudes the SZA during the overflight of the satellite is small (a more quantitative study will be the subject of the next section.). For the whole year a pronounced latitudinal variation is found (see also Figures 6.2 and 6.3), with the lowest BrO VCDs around the equator and the highest values towards the poles. At high and mid latitudes also a seasonal variation is obvious. The largest values (around $7 \cdot 10^{13}$ molec/cm²) appear during spring and the lowest values during summer. In the tropics only a weaker seasonal variation is found which is overlaid by a much shorter variability with a period of about one to two months.
In Figures 6.2 and 6.3 it can be seen that the dependence of the BrO VCD from latitude is almost symmetrical around the equator. Another interesting feature is that the BrO VCDs at a certain latitude vary within a range of about $3 \cdot 10^{13}$ molec/cm² during the year. This variation is found to be nearly independent from latitude.

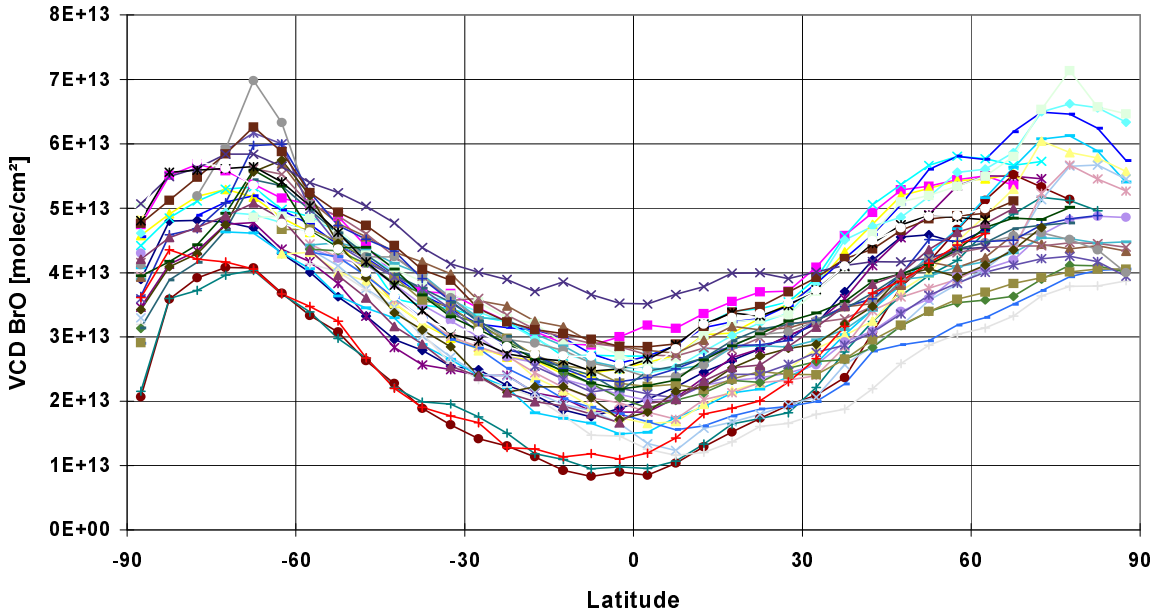


Figure 6.2 Summary of the latitudinal variation of the BrO VCD measured by GOME during 1997. Displayed are global 30-day averages every 10 days. The values are averaged also for latitude bands covering 5 degrees. It can be seen that the amplitude of the latitudinal variation is very similar for the whole year. However, the values differ by a nearly constant offset up to about more than $3 \cdot 10^{13}$ molec/cm².

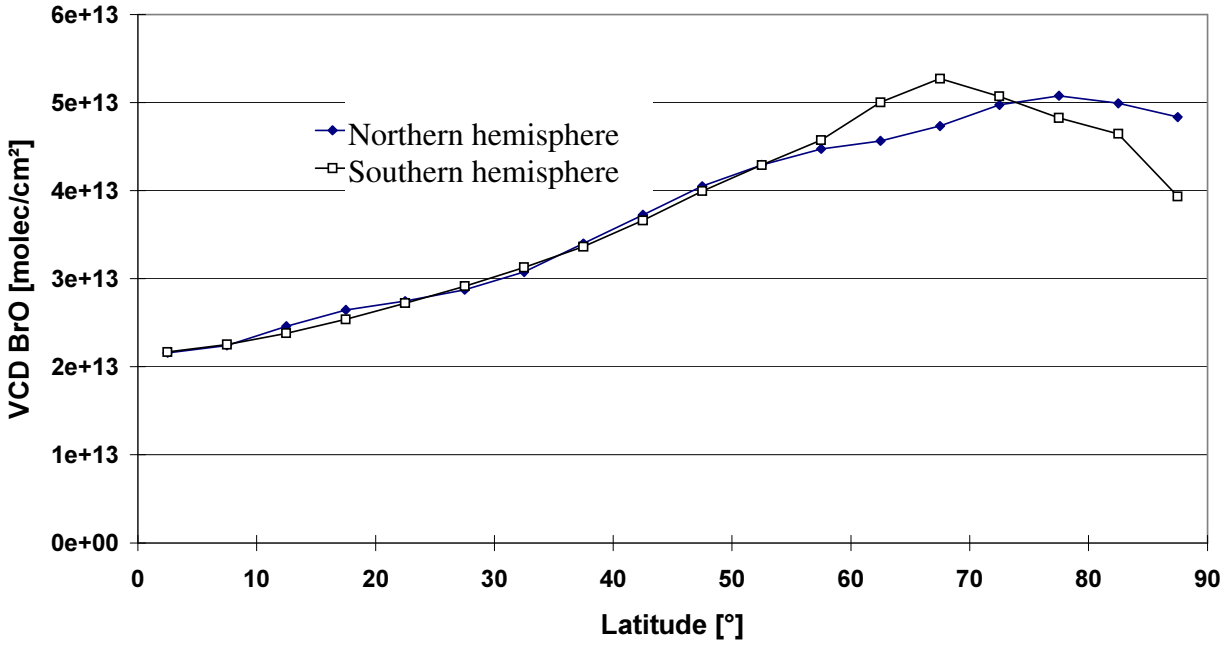


Figure 6.3 Yearly average of the BrO VCD measured by GOME in both hemispheres during 1997. The differences at high latitudes can be explained by the different latitudinal distribution of events of enhanced boundary layer BrO concentrations in both hemispheres (see section 6.3.5.3).

6.2 Stratospheric BrO

While in previous years it was generally believed that the atmospheric BrO was exclusively located in the stratosphere the present understanding includes also the occasional occurrence of BrO in the boundary layer and probably also in the free troposphere. Since GOME (and ground based instruments) measures the total atmospheric BrO column density, also the tropospheric column contributes to the measured BrO column densities.
In this section we compare the purely stratospheric BrO SCDs calculated for the profiles described in section 5.2.1 to the total BrO SCDs measured by GOME.
As shown in Table 6.1 the variation of the BrO VCD for the different profiles can be up to about a factor of 6 according (as an extreme case) to a change of the tropopause height from 6 to 18 km. In particular, at high latitudes and thus low tropopause heights the BrO VCDs are expected to be much larger than at lower latitudes, only because of the variation of the profile height. Despite from possible other effects this dependence can already qualitatively describe the observed dependence of the VCD BrO from the latitude quite well (see Figures 6.1, 6.2 and 6.3).
However, to investigate the measured values more quantitatively also the dependence of the AMF from the assumed BrO profile (and thus the tropopause height) has to be taken into account (see section 5.3.1). Figure 6.4 shows the respective AMFs for different tropopause heights (top) as well as the resulting SCD BrO, i.e. the AMF for a specific profile is multiplied with the corresponding BrO VCD (Table 6.1). At mid latitudes and the Tropics the variation of the resulting BrO SCD is as large as of the variation of the BrO VCD itself (Table 6.1). Fortunately, at high latitudes and thus large SZA the dependence of the BrO VCD and the AMF from the assumed BrO profile compensate each other to a large degree.

Tropopause height [km]	BrO VCD [10^{13} molec/cm²]
6	6.90
8	5.06
10	3.69
12	2.71
14	1.98
16	1.45
18	1.07

Table 6.1 BrO VCD for different tropopause heights under the assumption that the BrO mixing ratio increases from values around zero to 12 ppt within the first 10 km above the tropopause (see also Figure 5.4, section 5.2.1).

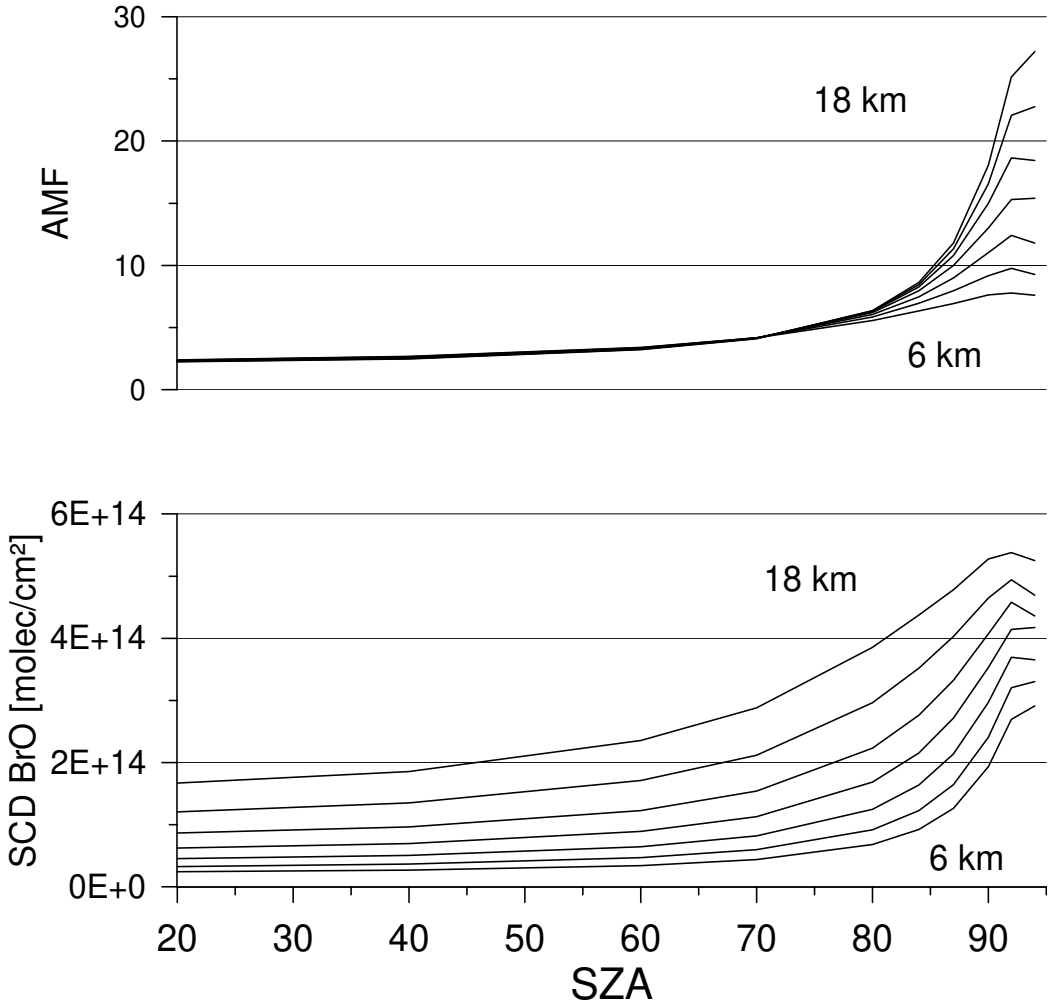


Figure 6.4 Top: AMF for Stratospheric BrO for different tropopause as described in section 5.2.1 as a function of the SZA. Bottom: SCD BrO resulting if the AMF for a specific tropopause height is multiplied with the corresponding BrO VCD (see Table 6.1).

In Figures 6.4 and 6.5 the measured BrO SCDs are compared to the calculated stratospheric BrO SCDs for different periods in 1997.
Figure 6.5 shows some latitudinal cross sections of the BrO SCD for different periods of the year 1997 when very low BrO SCDs were measured. This was in particular the case for March, June and December (slightly higher minima were also found for other periods). Also presented in Figure 6.5 are the calculated BrO SCDs for the BrO profiles according to tropopause heights of 8, 12, and 18 km. For all of the three cases the measured BrO SCD in the Tropics approach the values calculated for an altitude of the tropopause of 18 km but never drops below this curve. Assuming that for these examples the measured SCD BrO only represents the purely stratospheric SCD we can conclude that the measurements are in agreement with the stratospheric height profile of the BrO mixing ratios as discussed in section 5.2.1.
Or in other words: we never see GOME BrO observations which would indicate that the stratospheric mixing ratios might be smaller than used for the calculation (increasing from zero to 12 ppt within the first 10 km above the tropopause).
However, it should be noted that we cannot rule out in general, that a possibly lower stratospheric BrO SCD could be compensated by absorptions caused by BrO located in the troposphere.
Regarding the BrO SCDs at higher latitudes we find that the measurements are mainly between the calculated values for tropopause heights of 8 and 12 km which is in good agreement with the expectations for those latitudes. Thus, also from the observations at these latitudes we see no indications that the stratospheric mixing ratios might be smaller than assumed.

In contrast, for some cases the BrO SCDs at high latitudes are even higher than the calculated BrO SCDs for a tropopause height of about 8 km. And indeed, this feature was found for most of the GOME measurements (see also Figure 6.2); some examples are presented in Figure 6.6.

This difference between the measured and calculated BrO SCDs could be caused by several reasons:

A) The tropopause is located deeper than 8 km (see Table 6.1). However, while for some specific measurements this might be true it is very unlikely here, since the GOME measurements were averaged over a period of about one month.

B) The BrO mixing ratios in the stratosphere are significantly higher than assumed above. While this cannot be ruled out it might be in contradiction with the observed low BrO SCDs in the Tropics as well as with several balloon observations. It should be noted that for many GOME measurements the BrO SCDs are even higher than those presented in Figure 6.5.

C) The enhancement might be caused by additional BrO concentrations located in the troposphere. This assumption is also confirmed by other findings (see below) and seems to be the most likely explanation for the observed high BrO SCD.

In particular, at high latitudes during springtime (for April in the northern hemisphere and September and October in the southern hemisphere, see Figure 6.6) the measured BrO SCD by far exceed the calculated values. This is coincident with the observation of enhanced BrO concentrations in the boundary layer for these latitudes and seasons (see section 6.3).

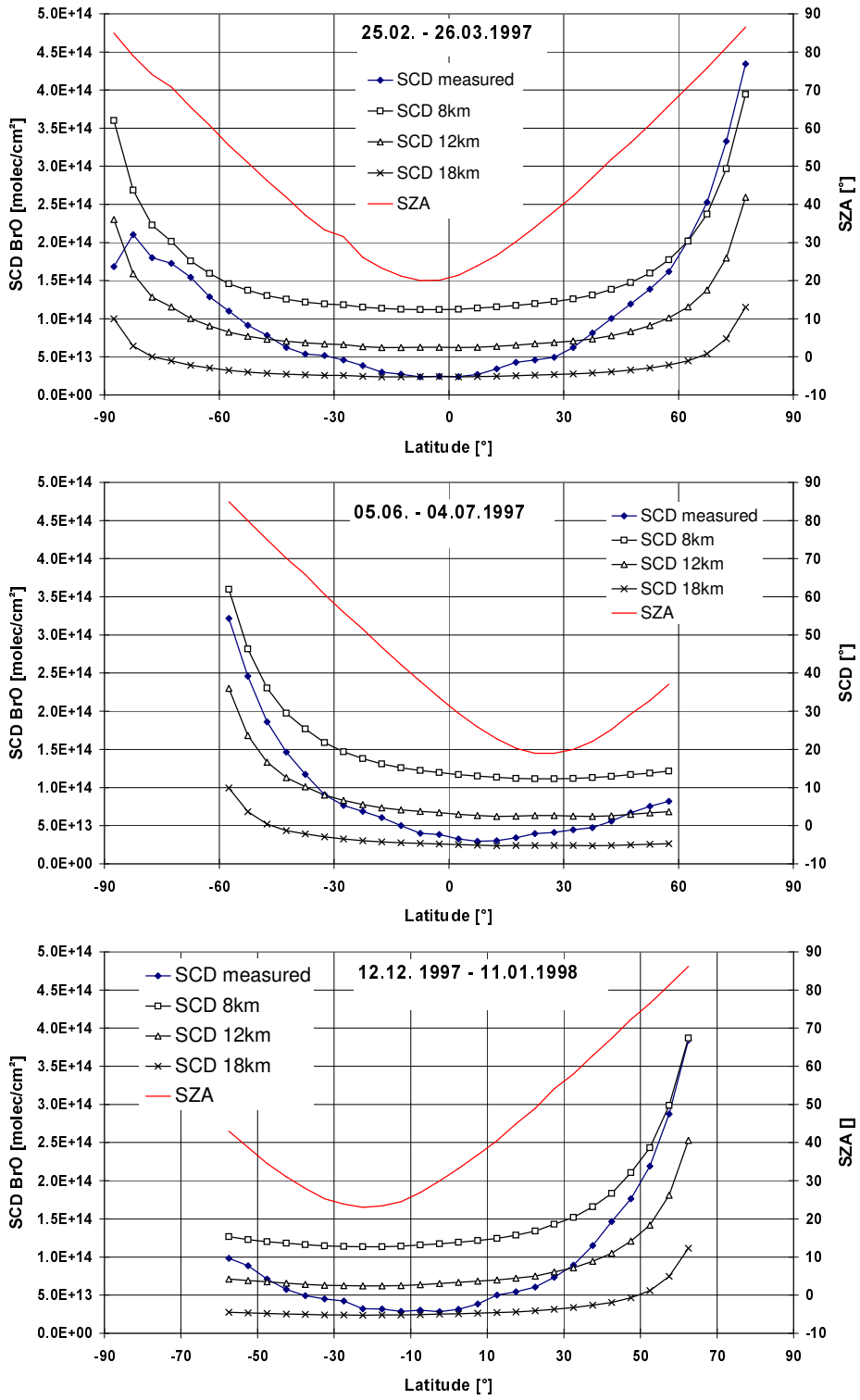


Figure 6.5 Latitudinal cross sections of the BrO SCD for different periods of the year 1997 when very low BrO SCDs were measured by GOME. Also presented are the calculated BrO SCDs for BrO profiles according to tropopause heights of 8, 12, and 18 km and the SZA for the GOME measurements. The measured BrO SCDs never fall below the calculated values.

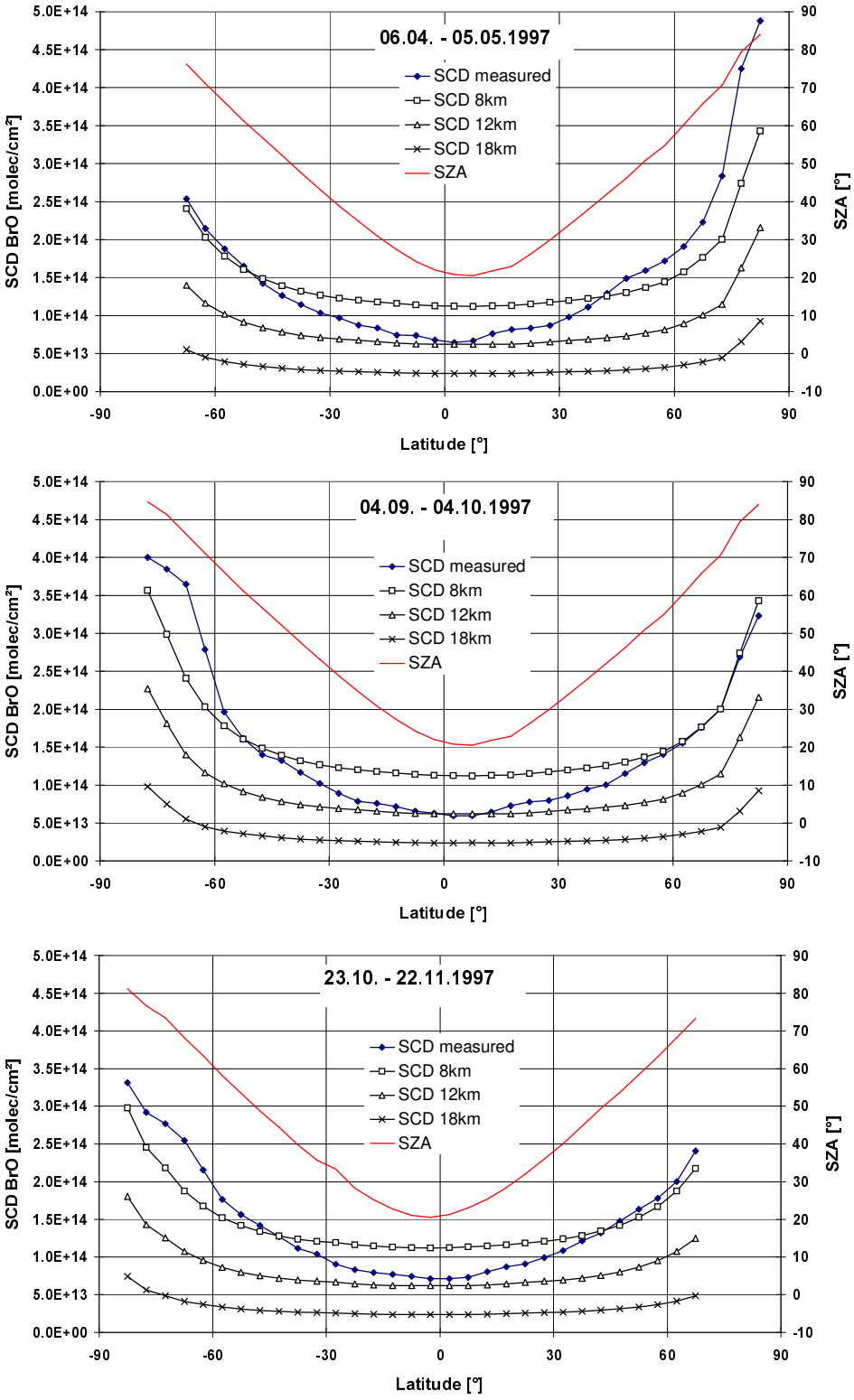


Figure 6.6 Latitudinal cross sections of the BrO SCD for different periods of the year 1997 when relatively high BrO SCDs were measured by GOME. Also presented are the calculated BrO SCDs for BrO profiles according to tropopause heights of 8, 12, and 18 km and the SZA for the GOME measurements. For most of the latitudes the measured BrO SCDs are significantly higher than the calculated values.

6.2.1 Summary of the GOME observations of stratospheric BrO

We developed a simple model for the stratospheric height profiles of the BrO mixing ratio with respect to the tropopause height (see also section 5.2.1). The resulting BrO SCDs for different latitudes were compared to BrO SCDs measured by GOME in 1997. The results of this comparison can be summarised as follows:

A) In most of the cases the GOME BrO measurements are significantly higher than the modelled SCDs. Thus we conclude that considerable BrO concentrations are present also in the troposphere. To explain the measurements with purely stratospheric BrO the stratospheric mixing ratios would have to be significantly higher than 12 ppt (this mixing ratio was used for the modelled BrO SCDs): up to about 16 ppt at high latitudes and up to about 24 ppt in the Tropics. The latter mixing ratio would even be higher than what is believed to be the total stratospheric content of bromine in the stratosphere.

B) No case was found for which the measured BrO SCDs were lower than the modelled ones. Assuming that for these observations only negligible tropospheric BrO concentrations are present this can be seen as an indication that the modelled stratospheric profiles are in agreement with the true stratospheric BrO mixing ratios.

6.3. BrO in the boundary layer

Hausmann and Platt [1994] presented the first observations of BrO in the planetary boundary layer during Arctic spring; these measurements were confirmed by several observations in the following years [Tuckermann et al, 1997; Martinez-Walter, 1999].
In the following sections we present GOME observations of BrO in the boundary layer during polar spring in both hemispheres.

6.3.1 Discovery

Within this PhD-thesis enhanced BrO concentrations in the polar boundary layer were detected by a satellite instrument for the first time [Wagner et al., 1998a; Wagner and Platt, 1998].
Fig. 6.7 shows the results for the southern part of one satellite orbit in which largely enhanced BrO absorptions were detected near 67°S, 161°E. While for SZA < 70° and > 78° the BrO VCD shows typical values for the atmospheric 'background', between 70° and 78° (shaded area) it is higher by a factor of 2 - 3 (Fig 6.7a). Also displayed in Fig. 6.7 are the absorptions due to O_2, the oxygen dimer $(O_2)_2$ (often referred to also as O_4), the SCD of NO_2 and O_3 as well as the measured light intensity (LI) averaged between 410 - 610 nm, and a colour index (CI, ratio of the intensities at 605 nm and 440 nm). The SCDs of the mainly stratospheric absorbers O_3 and NO_2 (Fig. 6.7d) show no significant change in the latitude range of the enhanced BrO absorption as it might be expected when the observed increase in the BrO concentration was due to a disturbance of the stratospheric composition.
Also the absorptions of O_2, $(O_2)_2$ as well as the LI and CI which are indicators for changes of the radiative properties of the atmosphere (e.g. due to clouds, see section 5.3), are essentially constant during the enhanced BrO absorption (Fig. 6.7b, c) making it unlikely that the enhanced BrO absorption was an artefact of possible radiative transport variations.

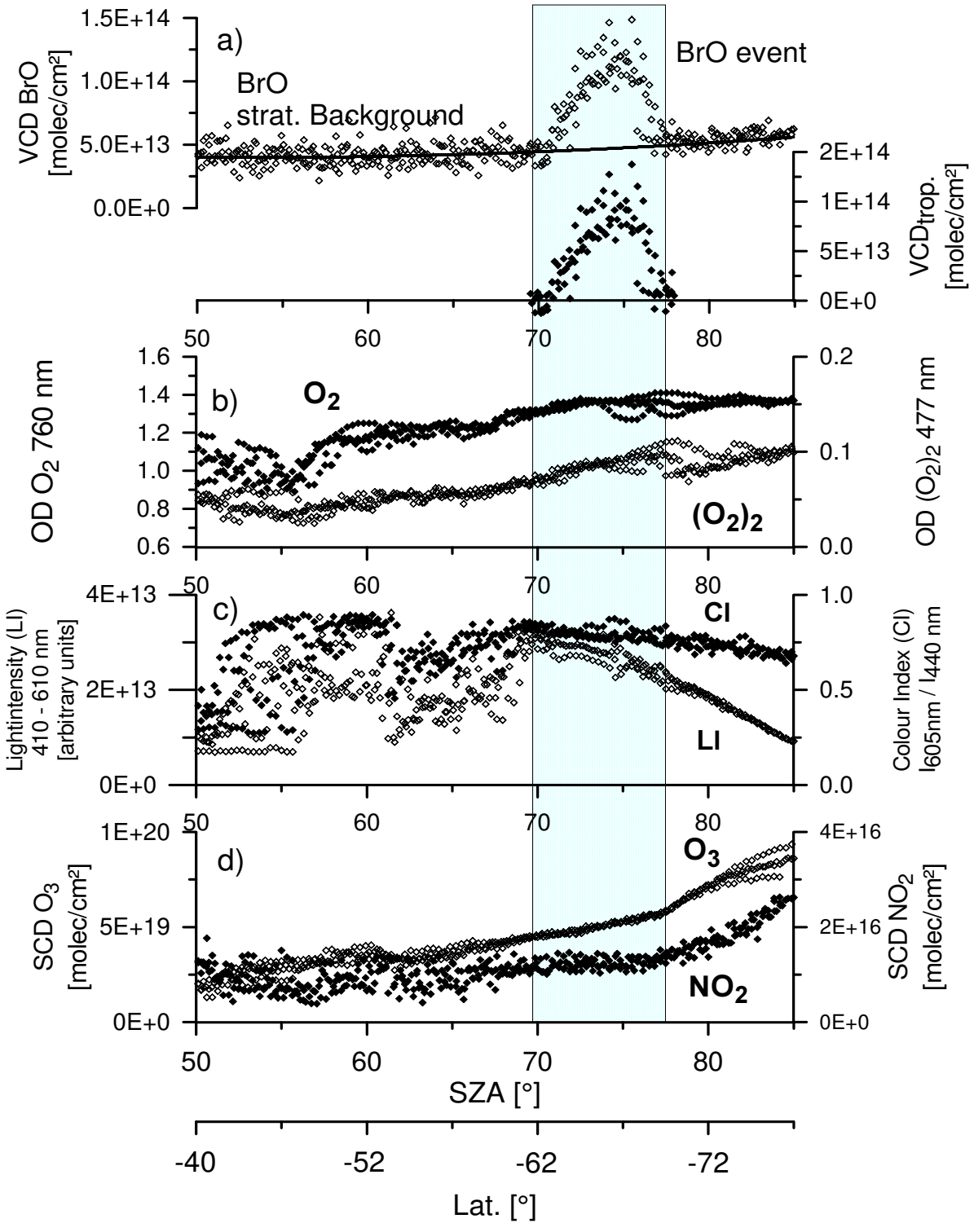


Figure 6.7 Latitudinal variation of the column densities of atmospheric trace gases, the average light intensity (LI) and a colour index (CI) for part of an orbit on September 15, 1996 (ERS-2 orbit 60915214). Also the tropospheric BrO VCD (black diamonds in Fig. 6.7a) calculated as described in the text is shown.

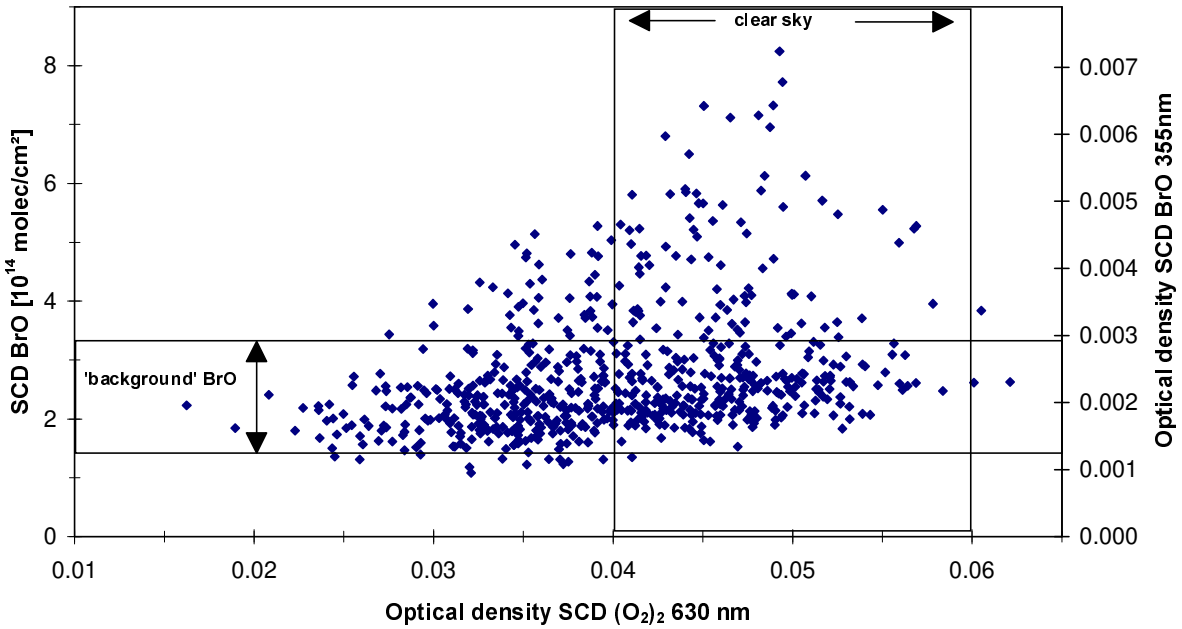


Figure 6.8 Scatter plot of simultaneously measured BrO- and $(O_2)_2$-SCDs[1] around the Antarctic for Sept. 2 to 15, 1996. The displayed data belong only to a small range of the SZA (between 71° and 79°); thus the measured changes cannot be referred to the SZA-dependence. The vertical box indicates the range of $(O_2)_2$ absorptions for clear sky conditions. The horizontal box indicates the range of purely 'background' BrO slant column densities. In the chosen latitude range between 63° S and 67° S several events of enhanced BrO absorption were detected.

To further investigate the influence of clouds on our observations the detected BrO SCDs are plotted as a function of the simultaneously measured $(O_2)_2$ absorption for a period from September 2 - 15, 1996 (Fig. 6.8). It can be seen that 'background' values of the BrO SCD were detected for all conditions, while enhanced SCD BrO were only detected when high $(O_2)_2$ SCDs indicated (at least partly) clear sky conditions (vertical box).
In summary we can attribute the BrO absorption enhancements measured by GOME to tropospheric BrO concentrations for several reasons:
A) The BrO amounts observed by far exceed the integrated stratospheric BrO column densities predicted by models. In fact the BrO column exceeds what is believed to be the total bromine column existing in the stratosphere.
B) Enhanced BrO absorptions were only detected when simultaneous high $(O_2)_2$ absorptions (see Fig. 6.8) indicated that the instrument could look deep down into the troposphere (i.e. that there prevailed largely cloud free conditions).
C) Large horizontal variations in BrO are unlikely to occur and persist in the stratosphere. In particular, the observed BrO variations do not correlate with changes of other mainly stratospheric species (O_3, NO_2, see Fig. 6.7d).
D) Enhanced BrO absorptions were detected for times and locations (in springtime at the border of the sea ice) typical for the occurrence of enhanced tropospheric BrO-concentrations as indicated by ground-based experiments [Hausmann and Platt, 1994; Tuckermann et al., 1997].

[1] Here the respective optical densities are displayed since for $(O_2)_2$ only the product of the equilibrium constant between the O_2- and O_4 concentration with the absorption cross section is known [Greenblatt et al., 1990].

6.3.2 Quantitative determination of the BrO concentration in the boundary layer

As pointed out in section 5.2.2 it is difficult to quantitatively assess tropospheric VCDs (and thus also the tropospheric concentrations) from measurements of a space borne instrument. This is mainly due to the large uncertainty of the tropospheric AMF (see section 5.2.2). These uncertainties are even larger when clouds are present which is nearly always the case for the large ground pixels measured by GOME.
And even if the true tropospheric BrO VCD could be determined there remain large uncertainties regarding the conversion of the BrO VCD into tropospheric concentrations because in most of the cases the height profile for the 'BrO layer' is not known. Second, large horizontal gradients of the BrO concentration can occur across a GOME pixel.
Because of these large uncertainties in general it was not the aim of this study to derive the precise numbers of the tropospheric BrO concentrations from GOME measurements.
Nevertheless, in principle the boundary layer BrO concentrations can be calculated from the difference of the observed BrO VCD and the background BrO $VCD_{background}$ (drawn line in Fig. 6.7a) by

$$VCD_{trop} = (VCD - VCD_{strat}) * AMF_{strat}/AMF_{trop} \quad (6.1)$$

This calculation makes use of AMF_{strat} and is thus based on the assumption that the 'background' BrO SCD is mainly located in the stratosphere which in general might not be true (see below). However, this should effect the derived BrO VCD_{trop} only negligible because AMF_{strat} is also used for the determination of the BrO VCD from the measured BrO SCD and thus cancels out applying Equation 6.1.
Table 6.2 summarises the BrO concentrations during several events of enhanced BrO in polar spring measured by GOME. With the assumption that the boundary layer reaches up to an altitude of 1000 m and that the BrO concentration is distributed uniformly within this layer we calculated BrO concentrations reaching up to about $1.3 \cdot 10^9$ molec/cm³ which is in good agreement with BrO levels up to $0.9 \cdot 10^9$ molec/cm³ found in 'DOAS long path' ground-based observations [Hausmann and Platt, 1994; Tuckermann et al., 1997]. A more detailed comparison is the subject of the following section.

Date of start 1996	Approx. duration (days)	Location (centre)	Max. BrO concentration* [10^8 molec/cm³]	Extension North-South (km)	Extension East-West (km)
Sept. 5	3	150°W, 67°S	12.9	1000	1400
Sept. 7	3	155°O, 67°S	10.1	600	700
Sept. 11	2	180°W, 69°S	5.7	400	1400
Sept. 15	2	160°O, 66°S	9.5	700	2000
Sept. 16	1	177°O, 68°S	5.9	300	300
Sept. 17	3	160°W, 74°S	5.7	1200	700
1997					
Apr. 20	2	30°W, 79°N	5.4	700	600

* if a BrO layer height of 1000 m is assumed.

Table 6.2 Summary of events of enhanced tropospheric BrO concentrations.

6.3.3 Comparison to ground based observations of O_3 and BrO

In this section we will compare the BrO data from GOME data with in-situ measurements of BrO and O_3 made at Spitsbergen.

6.3.3.2 Comparison of GOME BrO to in-situ BrO observations at Spitsbergen

During spring 1995 and 1996 'long path' DOAS measurements of boundary layer BrO were carried out at Ny Alesund, Spitsbergen [Tuckermann et al., 1997].
Table 6.3 shows the BrO concentrations measured from ground for several events of enhanced BrO concentrations during 1996 [Tuckermann et al., 1997]. Also displayed are the tropospheric BrO VCDs observed simultaneously by GOME.
Compared to the values listed in Table 6.2 the BrO concentrations and the BrO VCDs are significantly smaller at Spitsbergen and accordingly the relative error of the tropospheric BrO VCDs derived from GOME observations using the method described in section 6.3.2 is relatively large (about 50%).
Nevertheless, both data sets are in good agreement for assumed layer heights up to about 700 m. This is in good agreement with observations of the boundary layer in polar regions [Platt and Lehrer, 1996; Fortuin and Orlemans, 1992]. It in particular indicates that the observed BrO concentrations are present in the boundary layer rather than the whole troposphere.

Date 1996	trop. VCD BrO GOME [molec/cm²]	BrO concentration ground based meas. [molec/cm³]	resulting Layer height	Cloud properties from Satellite images 13:00 UT
07.04	0 (16:03 UT)	$2 \cdot 10^8$	0 m	partly cloud free
04.05.	$1.2 \cdot 10^{13}$ (15:15 UT)	$2 \cdot 10^8$	600 m	mostly cloud free
04.05.	$0.75 \cdot 10^{13}$ (18:30 UT)	$3 \cdot 10^8$	250 m	mostly cloud free
06.05.	$1 \cdot 10^{13}$ (17:30 UT)	$1.5 \cdot 10^8$	666 m	mostly cloud free
07.05.	$0.5 \cdot 10^{13}$ (16:03 UT)	$2 \cdot 10^8$	250 m	mostly cloud free
12.05.	$1 \cdot 10^{13}$ (14:24 UT)	$1.5 \cdot 10^8$	666 m	mostly cloud free
12.05.	$1 \cdot 10^{13}$ (17:40 UT)	$1.5 \cdot 10^8$	666 m	mostly cloud free
13.05.	$0.5 \cdot 10^{13}$ (17:11 UT)	$1 \cdot 10^8$	500 m	mostly cloud free

Table 6.3 Comparison of GOME and ground based observations during events of enhanced BrO concentrations in the troposphere. For the cases which were mostly cloud free both data sets are in good agreement for a BrO layer height of up to about 700m. The ground based data were taken from Tuckermann et al. [1997], the cloud cover was estimated from satellite images [Dundee, 1999].

6.3.3.2 Comparison of GOME BrO to in-situ O_3 observations at Spitsbergen

In this section we compare the GOME BrO data to in-situ measurements of O_3 in the boundary layer (Figure 6.9) performed at Spitsbergen by the Norwegian Institute for air research (NILU) (Harald J. Beine, personal communication). These measurements are described in more detail in Solberg et al. [1994].
While typical O_3 mixing ratios are about 40 to 50 ppb around April 17, April 21, April 26 and May 12 events of nearly total O_3 depletion were observed. Further events of less pronounced but sill strong O_3 depletion were also observed during April and May 1997. For all of these events enhanced BrO VCDs could be found in the GOME data, one example is shown in Figure 6.10. During that event (April 19 and 20, 1997) Spitsbergen is located at the edge of a very large area of enhanced BrO VCDs extending nearly around the whole polar region. As will be shown in section 6.3.5.3 occasions with enhanced BrO VCDs above Spitsbergen are very rare. The cases presented in Figure 6.10 represent some of the strongest ones during 1997. Also further events (see Figure 6.18) are well correlated to the O_3 depletion events shown in Figure 6.9. A more detailed study of these very interesting period can be found in Lehrer [1999].

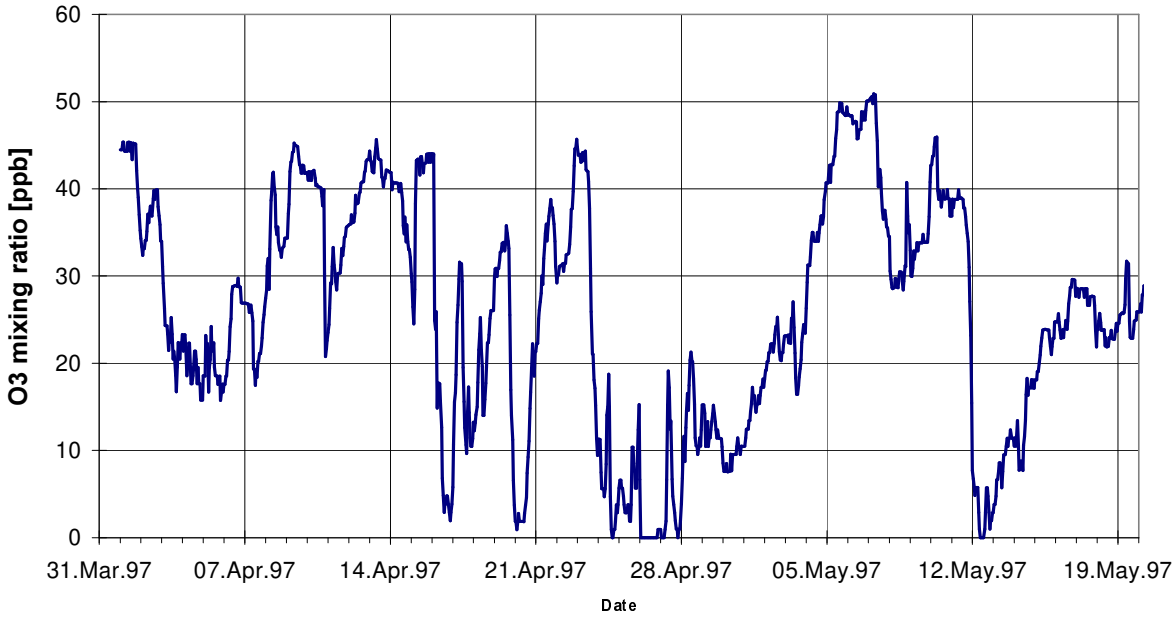


Figure 6.9 Time series of boundary layer ozone at the Zeppelin mountain at Ny Alesund (Spitsbergen) as described in Solberg et al. [1994] (Harald J. Beine, personal communication).

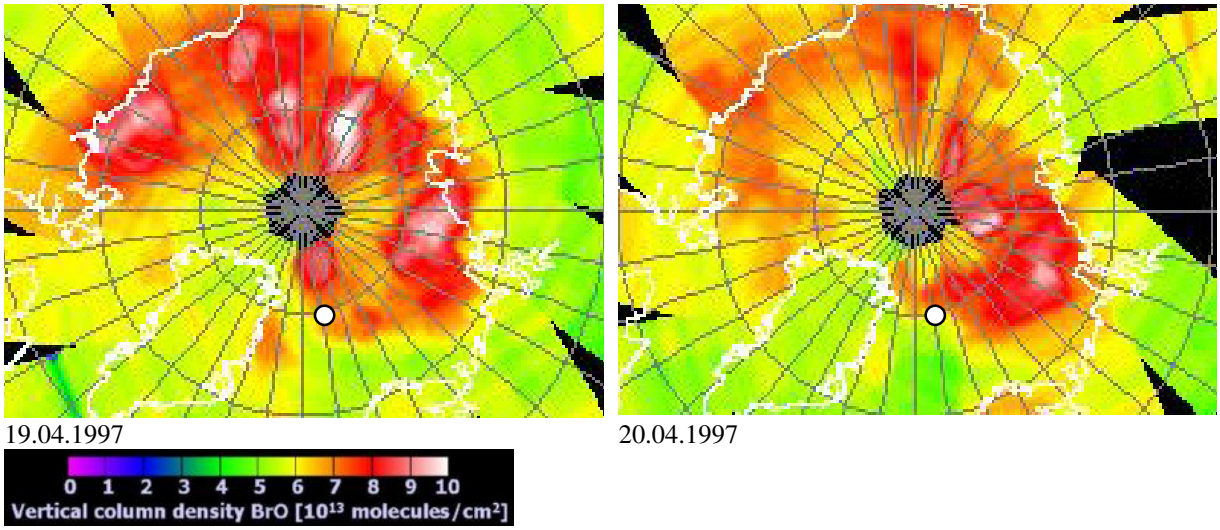


Figure 6.10 BrO VCDs in the Arctic for two days during April 1997 when strong tropospheric O_3 depletion events were observed simultaneously by ground based observations (see Figure 6.9). It can be seen that the area of enhanced BrO VCDs nearly surrounds the whole polar region, including in particular Spitsbergen, where the O_3 observations were measured. The green and yellow colours represent typical 'background' values (mainly located in the stratosphere and possibly also in the free troposphere) orange, red and white colours indicate areas of enhanced BrO VCDs.

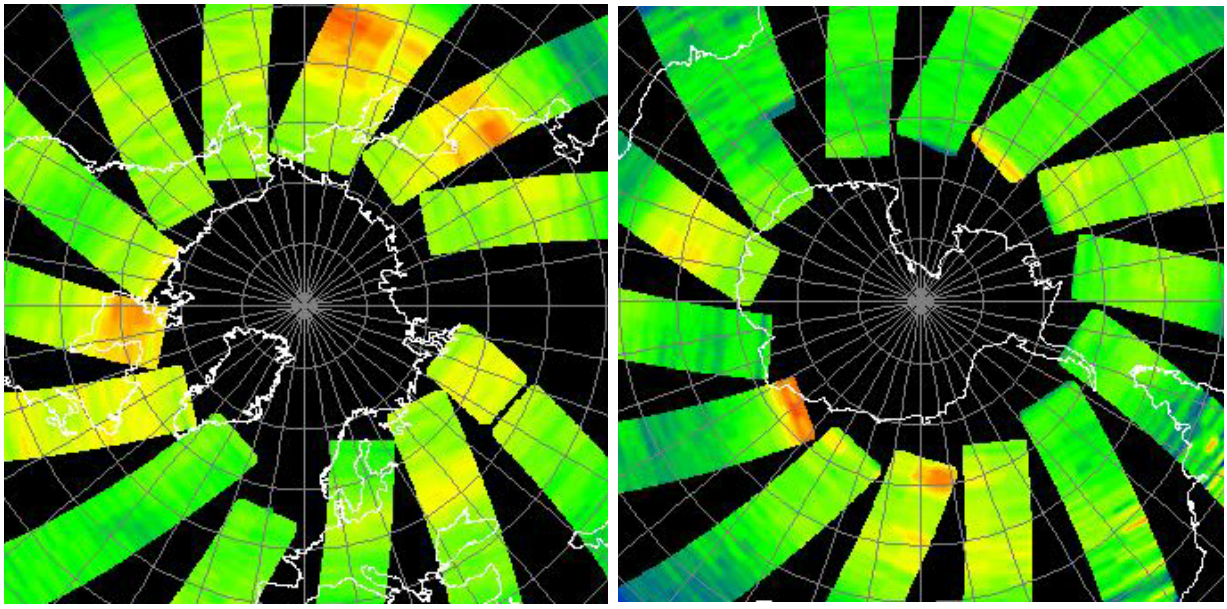
6.3.4 Examples of polar boundary layer BrO events observed in 1997

In this section we present some examples of typical GOME observations of enhanced tropospheric BrO concentrations during polar spring in both hemispheres. We selected events of enhanced boundary layer BrO for the beginning and the end of the period when such events occur. Also presented are examples of days when very large BrO concentrations occurred and the enhanced BrO concentrations covered very large areas.
The results presented in this section are derived applying the pure stratospheric AMF rather than applying equation 6.1. Thus a systematic dependence of the results from the SZA is introduced. We chose this approach for several reasons:
A) A quantitative assessment of the true BrO concentration in the boundary layer from satellite observation is in general limited by several parameters, especially by the uncertainty of the AMF (see section 5.2.2). In addition, the retrieved BrO VCD_{trop} depends strongly on the cloud cover. It is impossible to consider all these parameters even if they were known (which is not the case). Thus the uncertainty of the determined BrO concentrations is in general dominated by these uncertainties which also show systematic dependencies on the latitude (for the ground albedo and clouds).
B) Many questions regarding the phenomenon of enhanced BrO concentrations in the boundary layer concern the properties necessary for its appearance (like location and time, or SZA) rather than the exact numbers of the BrO concentration.

However, it should be noted that in principle the BrO VCD_{trop} presented in this section might be underestimated towards high SZA.

Early events

The first indications for enhanced BrO VCDs in the polar regions are found around the beginning of January and July in the northern and southern hemisphere, respectively (see Figure 6.11). Compared to events in later periods only weak enhancements (up to about $2 \cdot 10^{13}$ molec/cm² are observed, and also smaller areas are covered. While in the southern hemisphere enhanced BrO VCDs appear closely to the edge of sea ice around the Antarctic in the northern hemisphere they are found also towards lower latitudes (down to about 40° North). This might be related to the different distribution of land and ocean in both hemispheres. However, it cannot be ruled out that at least part of this difference might be caused by the change of the tropospheric AMF for sea ice (high albedo) and ocean (small albedo), see section 5.2.2.

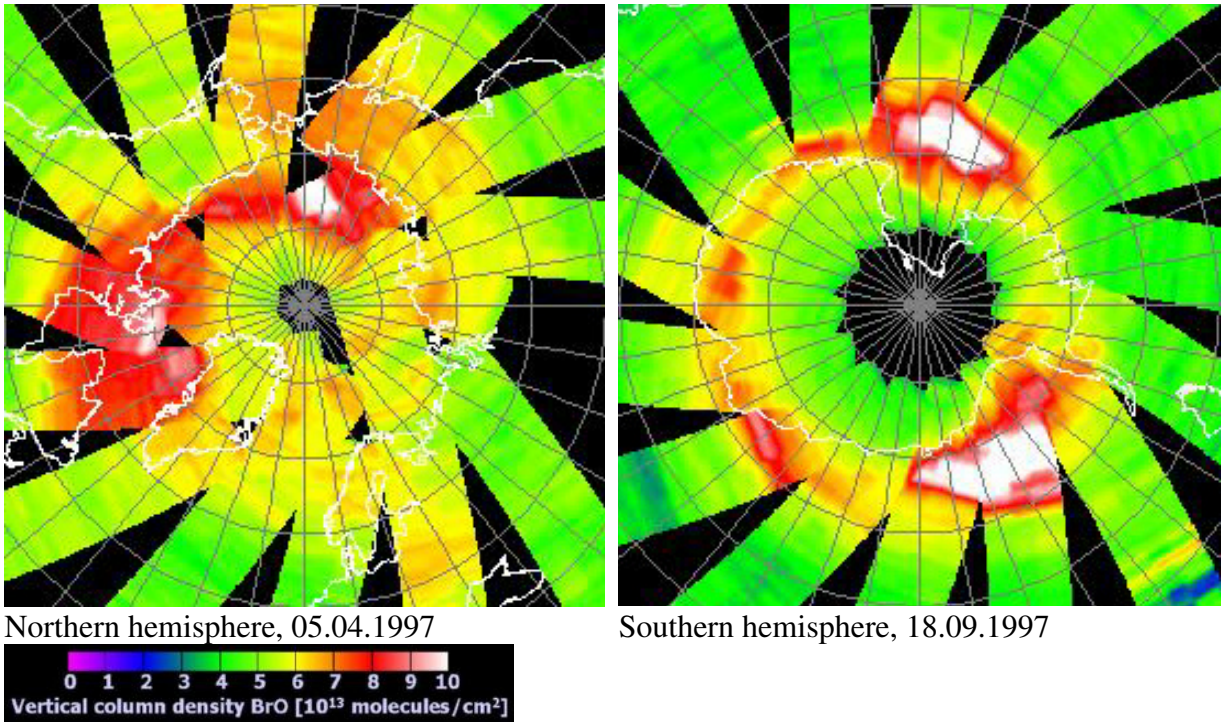


Northern hemisphere, 20.01.1997 Southern hemisphere, 08.08.1997

Figure 6.11 BrO VCD measured by GOME for the beginning of January and July when the first events of enhanced BrO VCDs appear in the northern and southern hemisphere, respectively. The green colours represent typical 'background' values (mainly located in the stratosphere and possibly also in the free troposphere), yellow and orange colours indicate areas of enhanced BrO VCDs due to BrO concentrations in the boundary layer.

Examples of high boundary layer BrO concentrations over large areas

The maximum enhancements of the BrO VCD are observed during March/April and August/September in the high latitudes in the northern and southern hemisphere, respectively. Thus, they occur about one month earlier around the Antarctic compared to the Arctic (with respect to the elevation of the sun). In both hemispheres often several separated areas or a very large area of enhanced BrO VCDs covering nearly the whole region surrounding the poles are simultaneously affected by high BrO (Figure 6.12).
In the southern hemisphere the enhanced BrO concentrations are typically located at the edge of the Antarctic; the boundaries of these areas usually show strong gradients. In contrast, in the northern hemisphere the areas of enhanced BrO VCDs show a much larger latitudinal variability. They are usually surrounded by areas with lower BrO VCDs rather than showing strong gradients. Typically, the maximum enhancements are smaller in the northern polar region compared to the southern polar region. In both hemispheres the areas of strong enhanced BrO VCDs are located above or near to areas which are covered with sea ice.

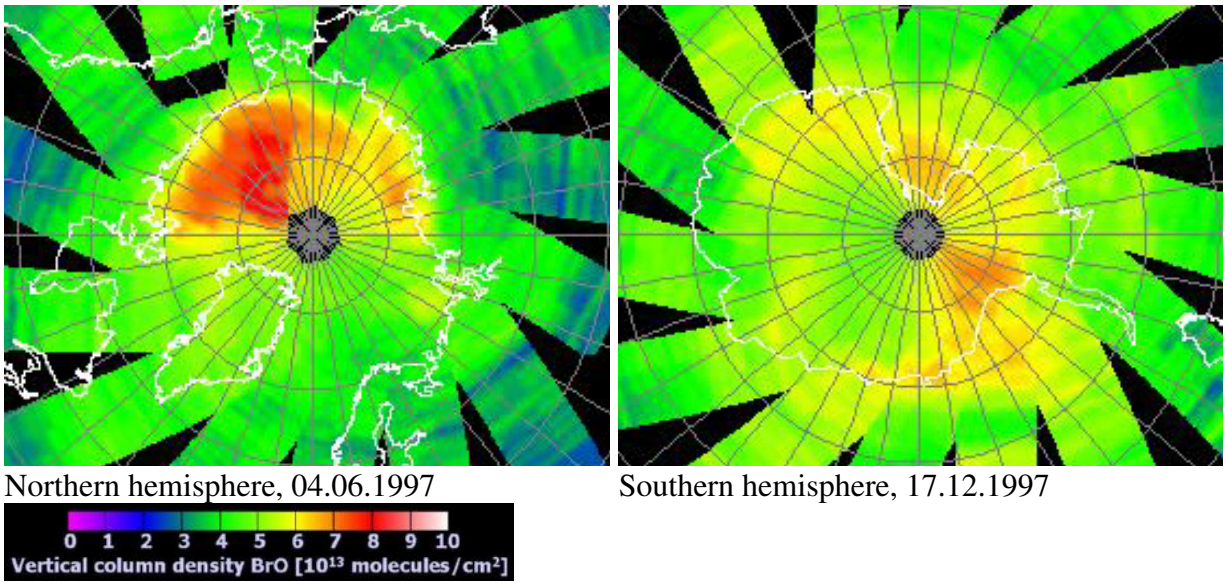


Northern hemisphere, 05.04.1997 Southern hemisphere, 18.09.1997

Figure 6.12 BrO VCDs measured by GOME during April and September when the strongest enhancement of the BrO VCDs occurred in the northern and southern hemisphere, respectively. The green colours represent typical 'background' values (mainly located in the stratosphere and possibly also in the free troposphere) orange, red and white colours indicate areas of enhanced BrO VCDs due to BrO concentrations in the boundary layer.

Late events

During June and December the latest events of enhanced BrO VCDs are observed in the northern and southern hemisphere, respectively (see Figure 6.13). For these periods the areas are located at high latitudes close to the poles. In the southern hemisphere the enhancements are weaker compared to the northern hemisphere.



Northern hemisphere, 04.06.1997 Southern hemisphere, 17.12.1997

Figure 6.13 BrO VCDs measured by GOME during June and December when the latest events of enhanced BrO VCDs were observed in the northern and southern hemisphere, respectively. The green colours represent typical 'background' values (mainly located in the stratosphere and possibly also in the free troposphere), yellow and orange colours indicate areas of enhanced BrO VCDs due to BrO concentrations in the boundary layer.

Examples of persistently enhanced boundary layer BrO concentrations

The enhanced BrO concentrations observed in the southern hemisphere typically last for a period of about one to three days. After short breaks in general they again form on the same place. In the northern hemisphere the situation is completely different: usually the BrO VCDs stay enhanced above particular areas up to several weeks, e.g. at the Hudson bay during March and April. However, also in the southern hemisphere cases with persistently enhanced BrO concentration can be observed. One example is shown in Figure 6.14.

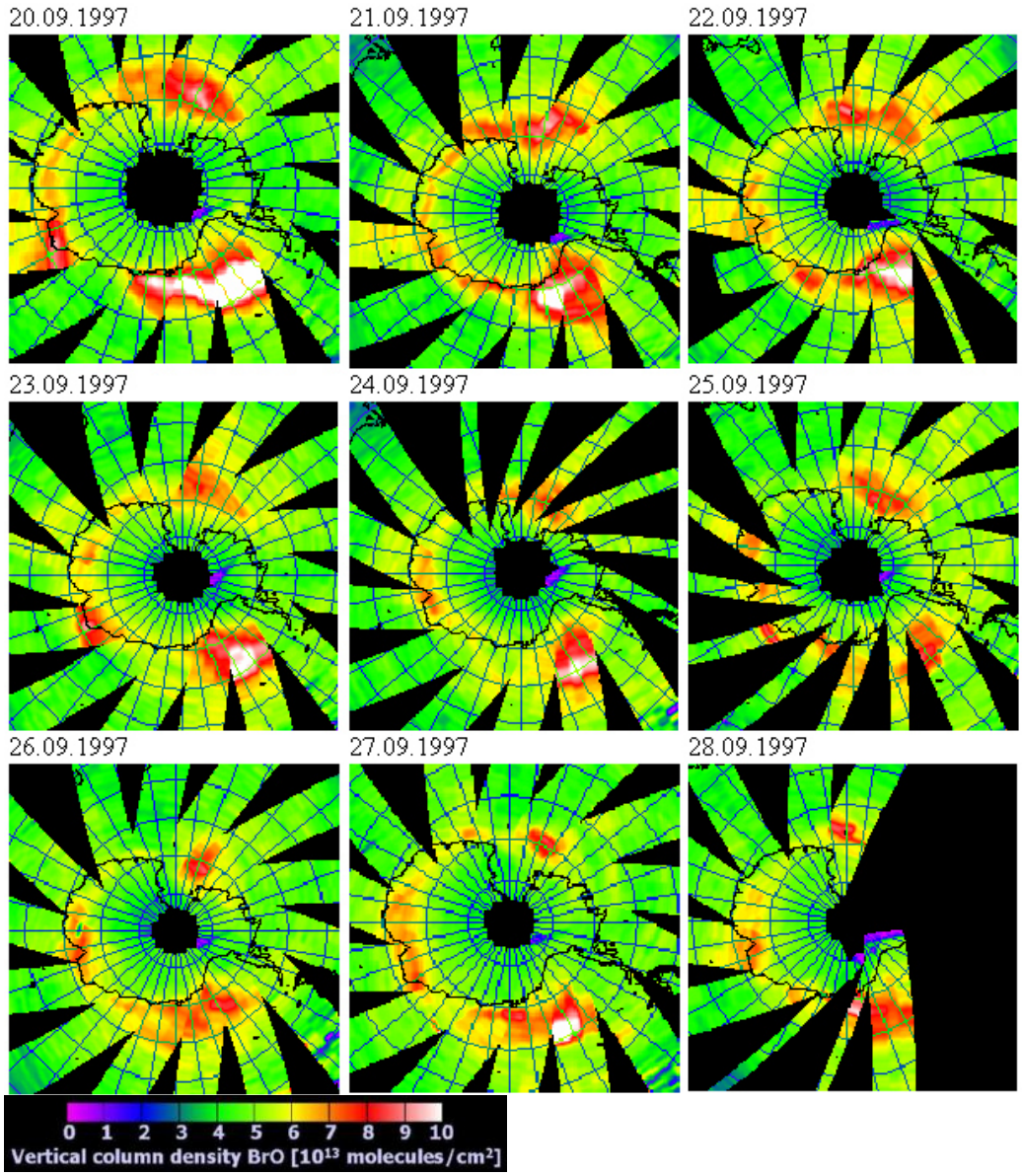


Figure 6.14 Time series of daily BrO VCDs around Antarctica from September, 20 to September, 28, 1997. The green colours represent typical 'background' values (mainly located in the stratosphere and possibly also in the free troposphere) orange, red and white colours indicate areas of enhanced BrO VCDs due to BrO concentrations in the boundary layer. Around 30° W, 65° S the enhanced BrO VCDs indicate a continuous occurrence of enhanced BrO concentrations in the boundary layer for more than a week.

6.3.5 Time series for both hemispheres

This section gives an overview of the temporal and spatial evolution of enhanced boundary layer BrO concentrations for both hemispheres.

6.3.5.1 Total area covered by boundary layer BrO

The temporal evolution of the total area of enhanced boundary layer BrO concentrations observed by GOME during 1997 is presented in Figure 6.15. In both hemispheres events of enhanced BrO can be observed during several months per year. Their duration is slightly longer (start slightly earlier and end slightly later) in the northern hemisphere. The total area of enhanced BrO concentrations in the northern polar region exceeds that of the southern polar region by about 20%. Compared to the southern hemisphere the tropospheric BrO VCDs are significantly smaller (by about 20%) in the northern hemisphere.

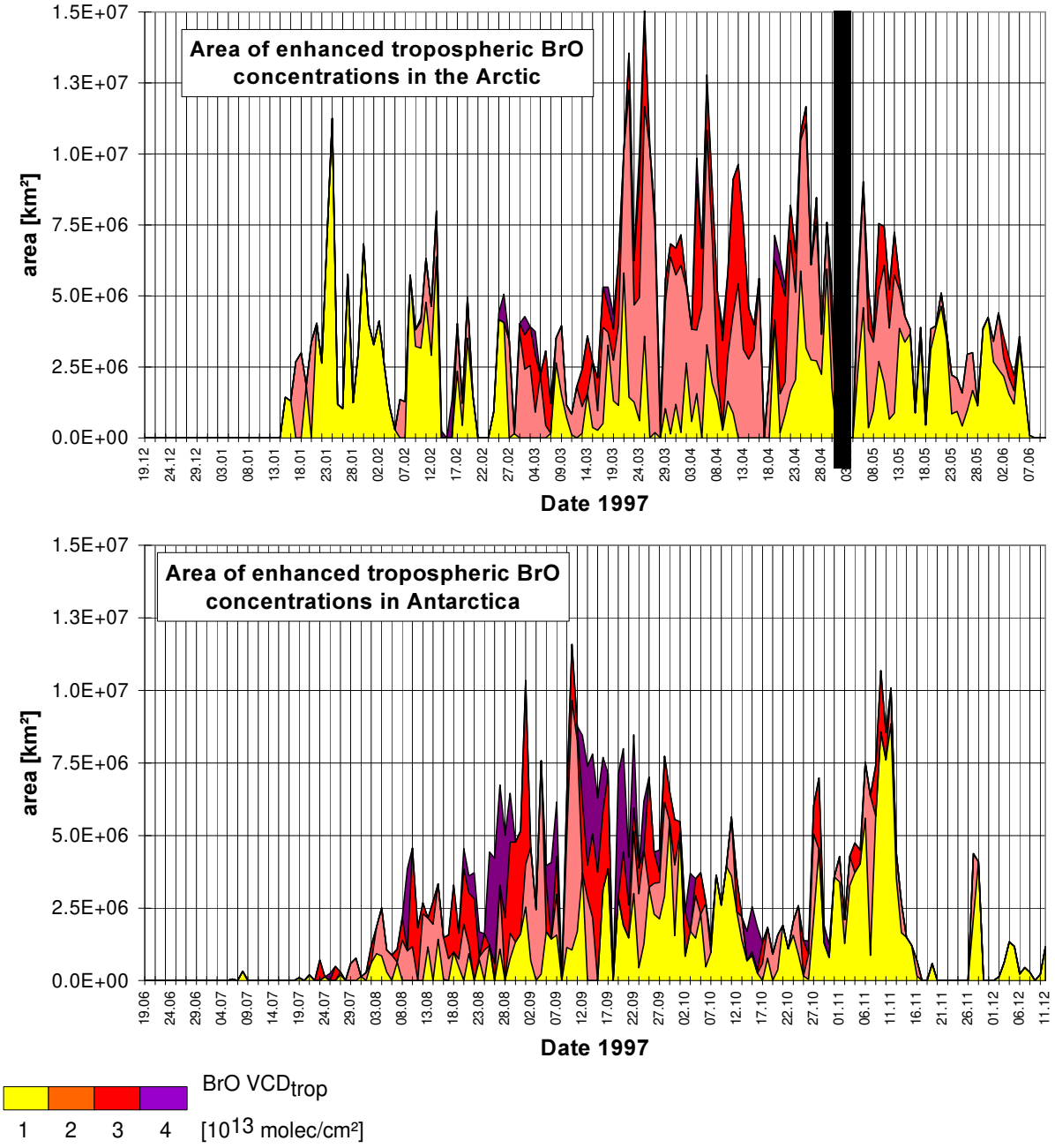


Figure 6.15 Temporal evolution of the total area where enhanced tropospheric BrO VCDs are observed by GOME for the northern (top) and southern hemisphere (bottom). The magnitude of the tropospheric BrO VCD is indicated by different colours. The black box indicates a period with no data.

6.3.5.2 Dependence on the latitude

Two important parameters change significantly during the period when enhanced BrO concentrations in the boundary layer can be observed: First, the sun's elevation which increases significantly from winter towards summer. Second, as a consequence of the rising sun, the temperatures increase towards the summer.

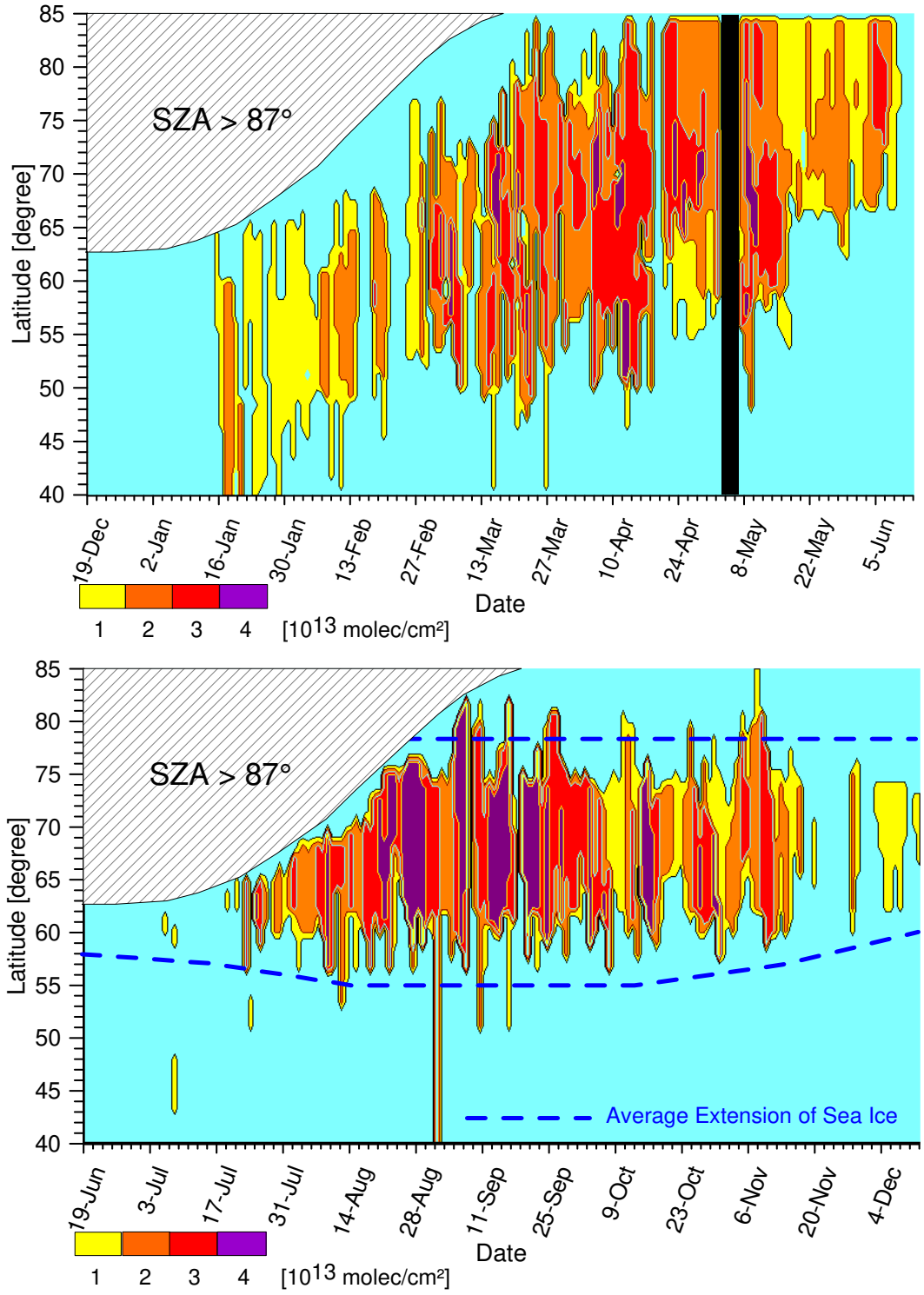


Figure 6.16 Tropospheric BrO VCDs (daily maximum values) as a function of latitude and time (top: northern, bottom: southern hemisphere). The magnitude of the tropospheric BrO VCD is indicated by different colours. Also shown is the typical extension of the sea ice surrounding the Antarctic (blue dashed line). The grey shaded areas indicate regions where the SZA for the GOME overpass is above 87°; these measurements were excluded as for these SZA the sensitivity of space-borne observations for species located in the boundary layer decreases strongly. The black box indicates a period with no data.

To study the possible impacts of these parameters on the boundary layer BrO concentrations the latitudinal variation of enhanced BrO concentrations as a function of time is investigated (see Figure 6.16).
In the southern hemisphere, for the whole period enhanced BrO VCDs can be seen within nearly the same latitude range (from about 58° to 77°S) which is closely related to the extension of the sea ice surrounding the Antarctic continent. In contrast, in the northern hemisphere a systematic dependence on the latitude is found: During January enhanced BrO VCDs are observed towards mid latitudes (down to below 40°N); in the following months this range shifts towards the pole. After mid March enhanced BrO VCDs can be found within a large latitudinal band extending from about 45° N to close to the pole. After the middle of May they are mainly found north of about 65°N.
These differences in both hemispheres seem to be most probably related to the extension of the regions covered by sea ice. While in the Antarctic the sea ice is confined within a restricted area between about 55° and 78° S, in the northern hemisphere it extends over a much larger latitudinal range e.g. at several bays at the edges of the continents.
In addition there also is a region inside the Eurasian continent where frozen salt water exists during winter and spring: The Caspian and the Aral Sea (see Figure 6.17). Also at this region enhanced BrO VCDs were observed during springtime (Figure 6.17).
Enhanced BrO VCDs were observed over a wide range of SZAs (from about 35° to about 88°). Thus the formation of enhanced BrO concentrations in the boundary layer seems to depend on the SZA only to a small extent. I.e. it probably forms even when there are only small amounts of sunlight.

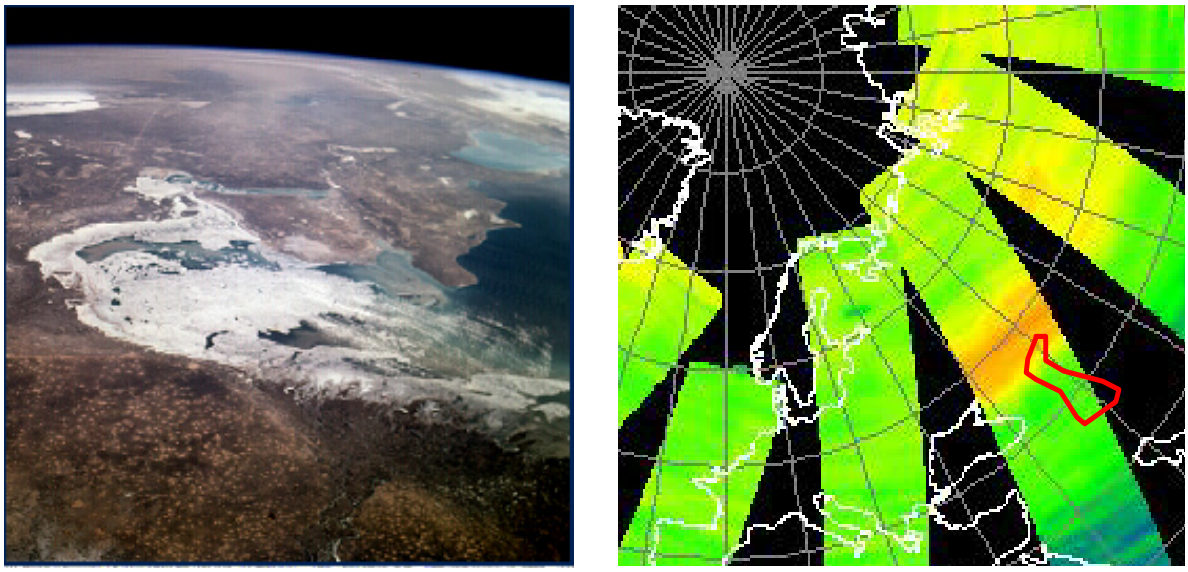


Figure 6.17 Left: Satellite view of the north-east corner of the Caspian Sea (looking south-east) during spring. The white patch near the upper left is the ice-covered Aral Sea. The northern part of the Caspian Sea is ice-bound, despite the heavy spring flow into the sea from the Ural and Volga Rivers. The hazy atmosphere near the background is due to dust blowing from a region near the Aral Sea (Satellite image taken from the NASA web site: http://eol.jsc.nasa.gov/newsletter/html_Mir/caspian.html, Responsible NASA Official: Dr. Kamlesh Lulla). Right: BrO VCD measured by GOME on March, 3, 1997. At the northern border of the Caspian sea (indicated by a red line) an extended area with enhanced BrO VCDs was observed.

6.3.5.3 Longitudinal distribution

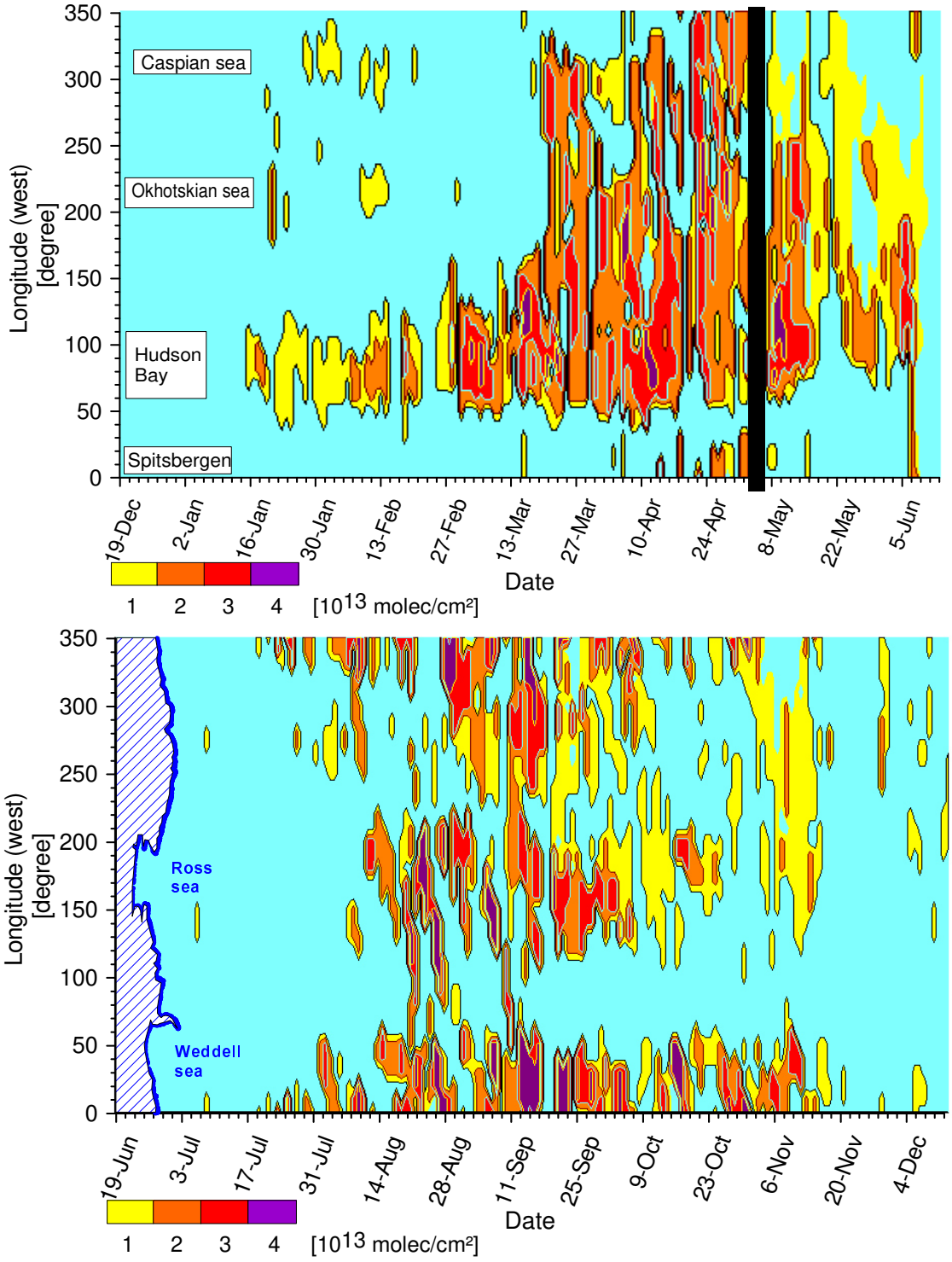


Figure 6.18 Tropospheric BrO VCD (daily maximum values) as a function of longitude and time (top: northern, bottom: southern hemisphere). The magnitude of the tropospheric BrO VCD is indicated by different colours.
For the northern hemisphere the latitude ranges of several important geographic areas are indicated; for the southern hemisphere the contour of the Antarctic continent is displayed. The black box indicates a period with no data.

For a given day the maximum elevation of the sun is similar for all locations at a specific latitude band. Thus, from the longitudinal distribution of enhanced BrO VCDs indications might be found as to which areas and conditions are favourable or necessary for the release of in the boundary layer. In Figure 6.18 the longitudinal distribution of enhanced BrO concentrations is shown as a function of time for both hemispheres.
Especially during the beginning of the period for which enhanced BrO VCDs were measured they mainly occurred at specific locations. In the northern hemisphere the most preferred region is the Hudson Bay (northern Canada), the Caspian Sea (Russia) as well as the Okhotskian sea (north of Japan). In the southern hemisphere enhanced BrO VCDs are mainly observed over the Weddell and the Ross Sea. Also for the following months most of these regions are frequently covered by enhanced BrO VCDs, however, for these periods enhanced BrO VCDs are also observed at other regions.
In both hemispheres specific regions exist where enhanced BrO VCDs were observed only rarely. In the northern hemisphere this is especially the case for the northern Atlantic between Greenland and Scandinavia. In particular over Spitsbergen (where several measurement campaigns related to tropospheric ozone depletion have been performed during the last years) only a few events of enhanced BrO VCDs have been found (which correlate very well with periods of boundary layer ozone depletion measured at Spitsbergen, see Figure 6.9). In the southern hemisphere a region with only very few events of enhanced BrO VCDs is located around the Antarctic peninsula where the latitudinal extension of the sea ice is relatively small.

6.3.5.4 Summary of the GOME observations of BrO in the boundary layer

From satellite observations it was possible to monitor the spatial and the temporal evolution of the phenomenon of enhanced BrO concentrations in the boundary layer on a global scale.
The main conclusions of our studies are summarised in the following points:

A) From GOME observations enhanced BrO concentrations in the boundary layer could be measured similar to those from ground based observations.

B) Enhanced BrO concentrations in the boundary layer are observed in coincidence with ozone depletion events.

C) The first events appear in January and July for the northern and southern hemisphere, respectively. The last events were observed during June and December. Thus, enhanced BrO concentrations in the boundary layer are present anywhere on Earth during the whole year.

D) The highest boundary layer BrO concentrations and their largest spatial extension occur during March/April and August/September in the northern and southern hemisphere, respectively. In the northern hemisphere the areas are by up to 20% larger compared to the southern hemisphere. To the contrary, in the southern hemispheres the BrO concentrations are higher than in the northern hemisphere.

E) Enhanced BrO concentrations are mainly observed over areas covered by sea ice. In particular over the Antarctic continent they are found only seldom. Also over the northern Atlantic between Greenland and Scandinavia events were observed only sporadically.

F) Also at mid latitudes (around the Caspian Sea) events of enhanced boundary layer BrO concentrations were found. These events are also related to the occurrence of salt water ice.

G) Over a wide range of SZAs (from about 35° to about 88°) enhanced boundary layer BrO concentrations are observed. Thus the formation of enhanced BrO concentrations in the boundary layer seems to depend on the SZA only to a small extent.

6.4. BrO in the free troposphere

While a long time it was thought that atmospheric BrO was located in the stratosphere, during recent years enhanced BrO concentrations have also been detected in the boundary layer (occasionally in polar regions during winter/spring and in the dead sea valley). Most recently, however, there have also been speculations about BrO in the free troposphere. This new concept of atmospheric BrO can be described by a 'three-layer model' [Platt et al., 1999].
The first indications for BrO in the free troposphere were yielded by the comparison of balloon and ground based observations (see e.g. Pundt [1997], Harder et al. [1998], Wagner et al. [1998b]). However, most recently, indications have also been found in chemical models and studies of the atmospheric dynamics in the tropical tropopause [Dvortsov et al., 1998 supporting the assumption that about 1 to 2 ppt BrO might exist in the free troposphere [McElroy et al., 1999; Platt et al., 1999]. Similar amounts have been derived from observations.
This section presents GOME BrO measurements supporting the presence of BrO in the free troposphere.

6.4.1 Comparison with balloon-borne measurements

BrO height profiles have been measured by different groups during the past years using spectrometers aboard balloon gondola [Harder et al., 1998; Pundt et al., 1999]. From these observations it is possible to derive the pure stratospheric BrO VCD (indeed up to now it has seemed to be impossible to determine BrO concentrations for the troposphere [Ferlemann, 1998; Harder, 1999]).
From the comparison of the stratospheric BrO VCD and the total atmospheric BrO VCD derived from GOME or ground based measurements the magnitude of a possible tropospheric BrO VCD can be investigated. Figure 6.19 shows the results of this comparison for several balloon soundings performed by different instruments [Pundt et al., 1999; Harder et al., 1998; Fitzenberger, pers. comm.] for different latitudes and seasons. It is important to note that the AMFs in all cases were calculated for the (stratospheric) BrO profile derived from the respective balloon observation.
As a general feature it turned out that the BrO VCDs measured by GOME observations are significantly larger than the pure stratospheric BrO VCDs for all balloon soundings. This is similar for both sets of balloon data. For the balloon soundings which were performed at (or near to) Kiruna also the BrO VCDs from ground based observations [Enell et al., 1998; Wagner et al., 1998f] were compared to the results from the balloon soundings (see also section 6.4.3). For cloudy days the BrO VCDs measured from ground are between the BrO VCDs measured from GOME and balloon indicating that the sensitivity of the ground based observations to tropospheric BrO concentrations is significantly decreased by clouds above the measuring site (see also section 6.4.3). Accordingly, the results for days on which the sky above Kiruna was cloud-free (see also Figure 6.20) the BrO VCDs measured from ground are even higher than the BrO VCDs derived from GOME.
In contrast to ground based measurements for which the sky above the instrument is either cloudy or clear, nearly all of the GOME ground pixels are partly covered by clouds and thus the sensitivity for tropospheric BrO concentrations is usually smaller compared to purely clear sky conditions.

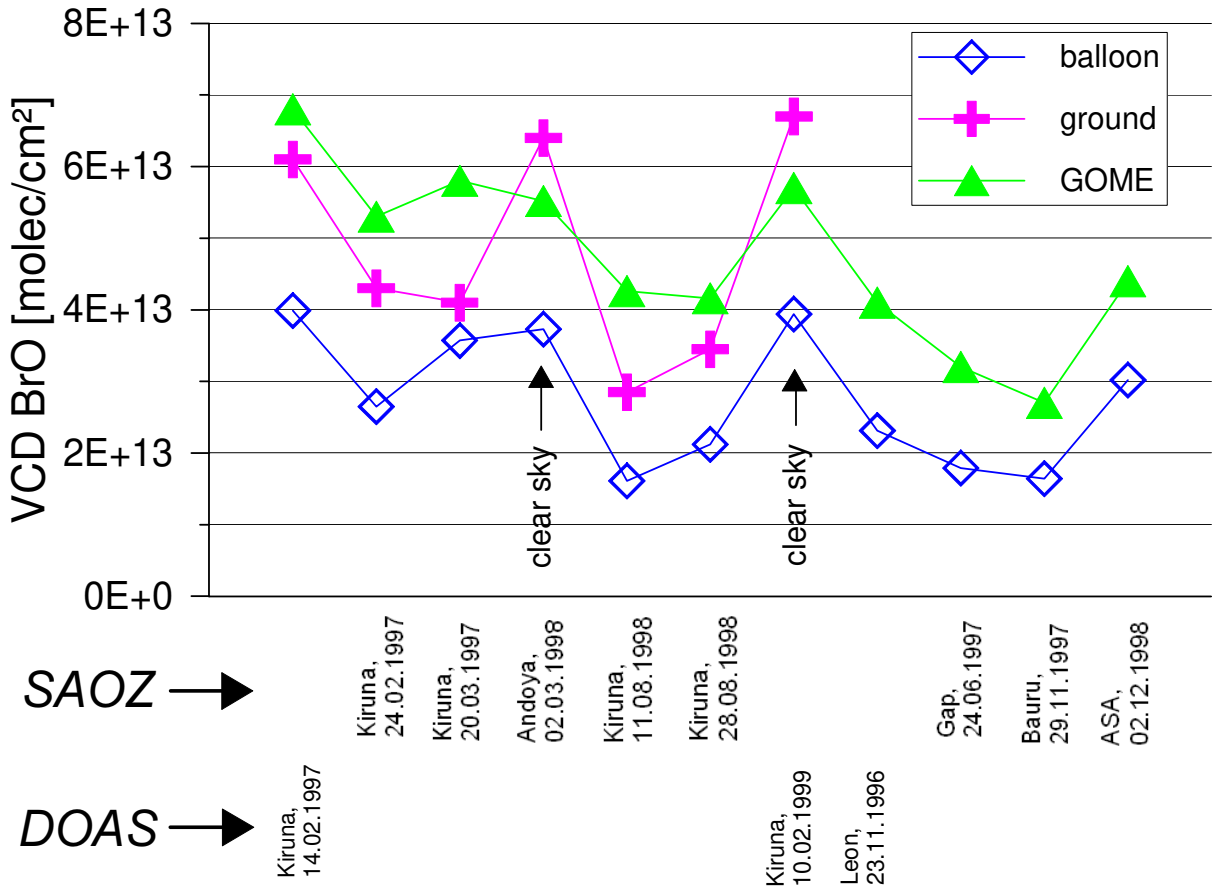


Figure 6.19 Comparison of stratospheric BrO VCDs from balloon borne observations measured with two different instruments (SAOZ [Pundt 1997; Pundt et al., 1999] and DOAS [Ferlemann, 1998; Harder et al., 1998, 1999]) with the total atmospheric BrO VCDs measured from GOME and a ground based instrument at Kiruna (the AMFs were calculated for the respective stratospheric BrO profile measured by the balloons). The balloon data are lower than the results from the other instruments for all cases. While GOME measurements are nearly always affected partly by clouds, the ground based observations strongly depend on the local cloud cover. For ground based observations on clear sky days (see also Figure 6.20) the results are even higher than those from GOME.

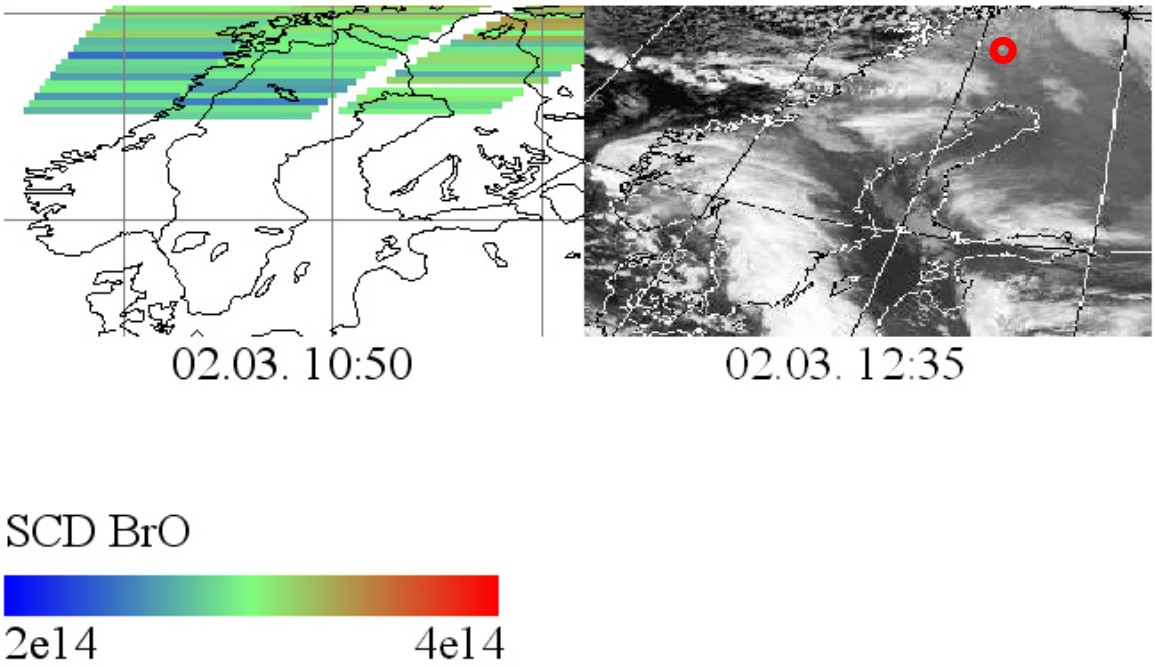


Figure 6.20 Left: GOME BrO VCDs for March, 2, 1998. Right: Satellite image for the same day [Dundee, 1999]. The sky above Kiruna where the ground based measurements were performed was clear while south-west and south-east clouds were present. For these regions decreased BrO VCDs were measured.

When comparing the results of these different instruments, the dependence of the atmospheric BrO concentration on the SZA has to be considered. This dependence can be investigated from ground based observations on a clear day for which the AMF is not influenced by clouds. In Figure 6.21 the diurnal variation of the BrO VCD measured at Kiruna for March 2, 1998 is shown using two different sets of AMF: The BrO VCDs in the upper panel are calculated assuming that all BrO was located in the stratosphere; the BrO VCDs in the lower panel are calculated assuming that BrO was also present in the troposphere. Displayed are also the BrO VCDs determined from GOME and balloon observations on the same day. It can be seen that the diurnal variation of BrO VCD depends strongly on whether it was assumed that BrO was in the troposphere or not. However, for both cases the BrO VCDs derived from the ground based observations are significantly larger than the pure stratospheric BrO VCD derived from the balloon measurement. This is a strong indication that BrO is actually present in the troposphere.
All measurements can be 'brought together' if it is assumed that a BrO mixing ratio of about 2.3 ppt takes place in the free troposphere. This assumption affects the results of the different measurements in the following way:
A) Ground based observations: The BrO VCDs are determined using the AMF for BrO also in the troposphere rather than only in the stratosphere.
B) Balloon observations: The integrated tropospheric concentration for an assumed mixing ratio of 2.3 ppt is added to the purely stratospheric BrO VCD measured by the balloon.
C) Satellite observations: The BrO VCDs are determined using the AMF for BrO also in the troposphere rather than only in the stratosphere. In addition it is assumed that clouds hide about 30% of the tropospheric BrO VCD corresponding to a cloud cover of about 50% (see Figure 6.20) and an assumed average cloud height of about 5 km (see also section 5.3.2).

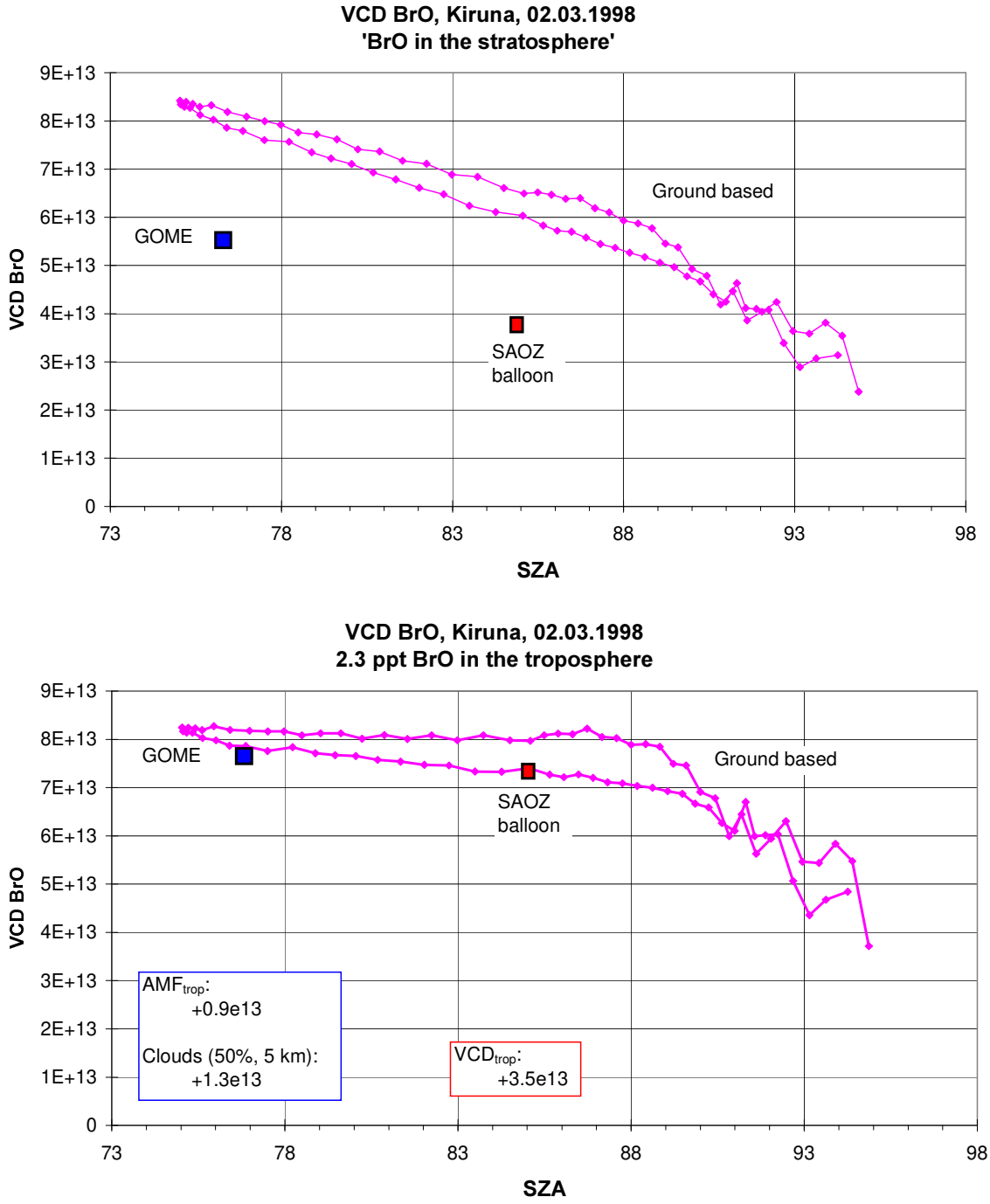


Figure 6.21 Comparison of the BrO VCDs from different instruments for a day which was cloud free at Kiruna where the ground based measurements took place. In the upper panel it was assumed that BrO was located in the stratosphere only, in the lower panel part of the BrO was assumed to be located also in the troposphere (with a constant mixing ratio of about 2.3 ppt). Since the AMFs strongly depend on the atmospheric profile, the BrO VCDs for the ground based observations (and also for the GOME measurement) differ significantly for both cases. For the GOME observation it was also taken into account that part of the tropospheric BrO was hidden by clouds. It can be seen that the different measurements can only be brought into agreement if a part of the atmospheric BrO is assumed to reside in the troposphere.

Assuming a BrO mixing ratio of 2.3 ppt in the free troposphere, the BrO VCDs from the ground based observation indicate that the BrO VCD for this day is nearly constant below a SZA of about 88°. The BrO VCDs displayed at the bottom of Figure 6.21 include the tropospheric part.

6.4.2 Comparison of the GOME BrO SCDs with GOME O_4 measurements

As already shown in Figure 6.20 an effect of clouds on the BrO VCDs can be found in GOME data, which is consistent with the assumption that part of the total atmospheric BrO VCD is located in the troposphere. To further investigate this effect we studied GOME measurements around the Tropics where usually clouds can reach high altitudes because of strong convection. Due to the large vertical extension of the troposphere at those latitudes the integrated tropospheric BrO VCD can also be expected to be large. Thus the measured total BrO VCD should be largely decreased when high clouds are present which hide the instrument's view down into the troposphere.
In Figure 6.22 the latitudinal dependence of the BrO SCD and the O_4 absorption measured by GOME are shown for several (arbitrarily selected) orbits at mid and low latitudes for all seasons. To study a possible sea-land dependence two data sets were selected, one above the Pacific and one above Africa.
While in most orbits there appears a broadband variation of both measured species which can be attributed to the dependence of the SCD from SZA, also many narrow variations are obvious. Since O_4 is mainly located near the Earth's surface (with a scale height of about 4 km), the changes of the O_4 absorption can be explained by a changing cloud cover (section 5.3.2). This relation can in particular be seen in Figure 5.18.
For many of the GOME observations over the ocean the BrO SCDs are significantly decreased when small O_4 absorptions are observed. This is in particular true for the Tropics, where the clouds can reach very high altitudes. This observation is consistent with the assumption that a significant part of the total atmospheric BrO VCD is located in the troposphere. One could argue that the cloud induced change of the albedo might decrease the stratospheric BrO AMF and thus explains the observed absorption decreases. But this is not the case (see also section 5.2.1). First, the dependence of the stratospheric AMF from such changes is rather weak compared to the observed variations. Moreover, it would even lead to an absorption increase in the presence of clouds.
Most of the observed decreases of the BrO SCDs are related to very strong absorption decreases of O_4 while for only weak absorption decreases of O_4 nearly no influence on the BrO SCD is found. This can be explained qualitatively by assuming that the tropospheric BrO is located near the tropopause rather than at lower altitudes. This was indeed found by a balloon observation in the Tropics [Pundt et al., 1999].
In contrast to the observations over the Pacific, above Africa the correlation between the O_4 and BrO is significantly lower. In addition, the BrO SCDs are in general smaller compared to the orbits over the ocean. These findings can be explained assuming that the tropospheric BrO concentrations is smaller over the continent compared to the ocean. It is important to note again, that this dependence cannot be explained by the dependence of the tropospheric AMF on the ground albedo which would cause the opposite effect (see section 5.22).

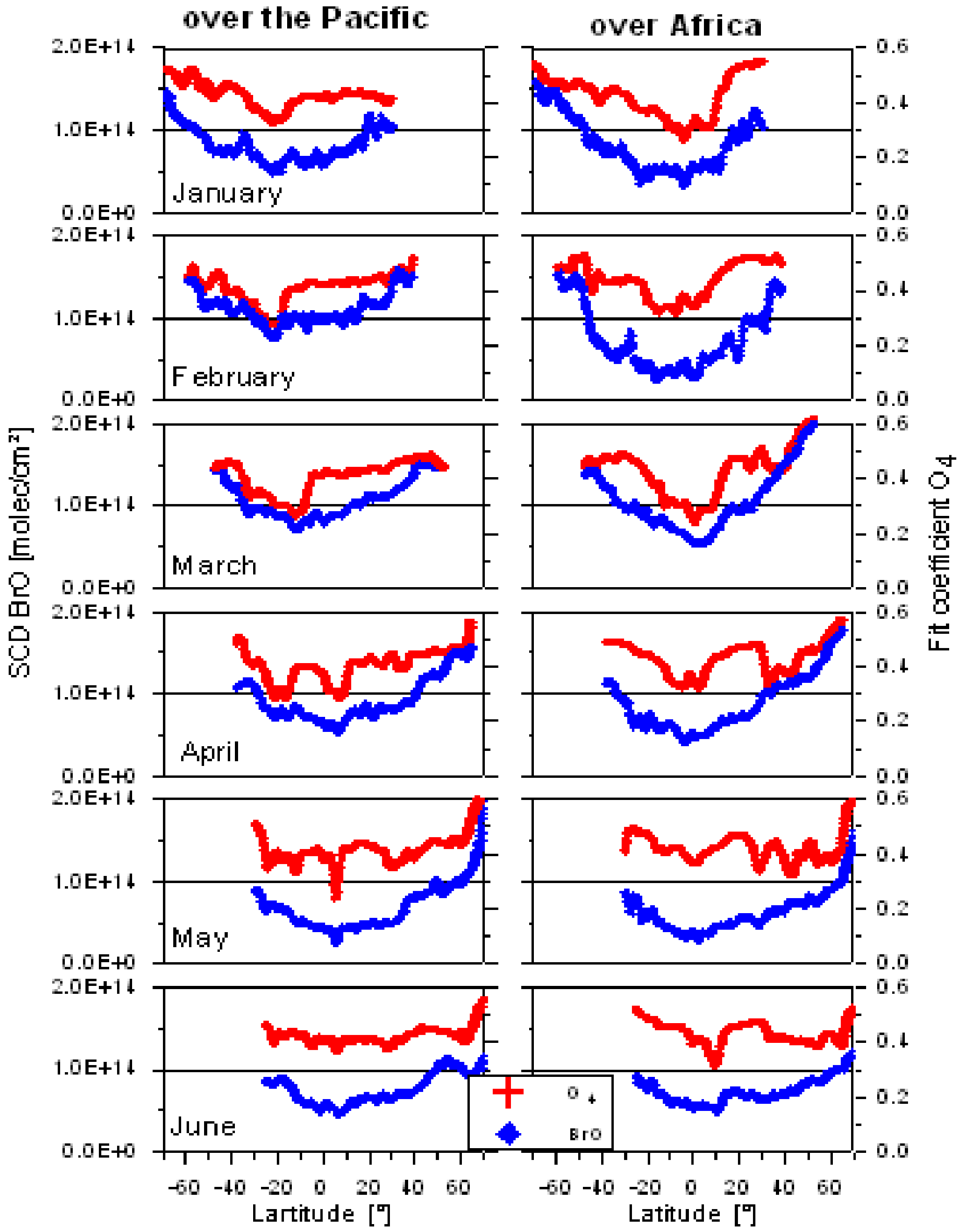


Figure 6.22 A Latitudinal dependence of the BrO SCD (blue curves) and the O_4 absorption (red curves) measured by GOME for several (arbitrarily selected) orbits for January to June 1997. Two data sets, one over the Pacific and one over Africa were chosen. To reduce the small-scale variations for the BrO SCD (see e.g. Figure 6.7), the data were smoothed (running average over 30 neighbouring measurements); only measurements for SZA below 60° were selected.

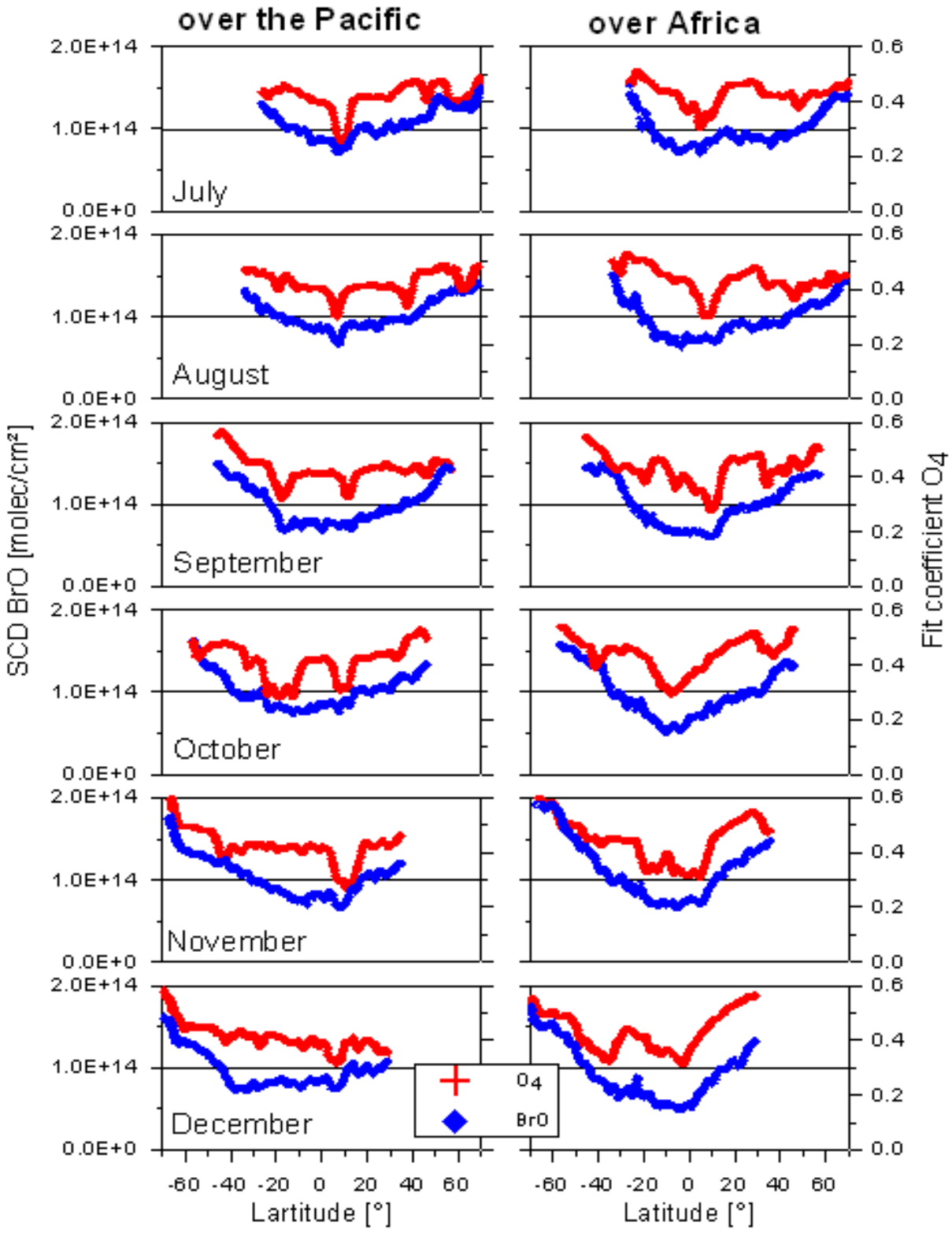


Figure 6.22 B Latitudinal dependence of the BrO SCD (blue curves) and the O_4 absorption (red curves) measured by GOME for several (arbitrarily selected) orbits for July to December 1997. Two data sets, one over the Pacific and one over Africa were chosen. To reduce the small-scale variations for the BrO SCD (see e.g. Figure 6.7), the data were smoothed (running average over 30 neighbouring measurements); only measurements for SZA below 60° were selected.

6.4.3 Comparison of GOME data with ground based BrO measurements

In section 6.4.1 BrO VCDs measured from ground were already compared to GOME observations for selected days when also balloon observations were performed. In this section this comparison is extended over a larger period from January to March 1997.
The GOME BrO data are compared to ground based DOAS measurements at the Institute for Space Physics (IRF) at Kiruna (Sweden) which have been performed since December 1996 in a co-operation with the Institute for Environmental Physics at the University of Heidelberg [Enell et al., 1998; Wagner et al., 1998f]. The instruments are described in detail in Otten et al. [1998] and Wagner et al. [1998e,].
From a comparison of the GOME data with ground based observations the temporal evolution can be studied with special emphasis on the dependence on the SZA. During the period of the comparison the SZA for the satellite overpass above Kiruna changes from about 90° in January to about 70° in March. This allows to study the influence of the SZA over a wide range. In addition, also different atmospheric conditions can be studied, which include 'ozone hole conditions' during winter and unperturbed conditions outside the vortex and towards summer.

The BrO evaluation for the ground based observations were performed in the same wavelength interval and using a similar set of reference spectra as for the GOME BrO analysis (see section 4.3.7). For the comparison GOME measurements were chosen for which the centre of the ground pixel was located within an interval of ±1° north/south and ±5° east/west of Kiruna (67.9°N, 21.1°E). From the ground based measurements spectra were selected which were measured at SZAs within ±0.5° with respect to the average SZA of the selected GOME measurements. For the selected measurements of both instruments the daily average of the SCD BrO of the selected measurements was calculated. Accordingly, the respective AMF for the average of the SZAs was applied.

In Figure 6.23 the VCD BrO for both sets of measurements is shown (for these data an AMF for a profile height of 14 km was used, see supplement A). It can be seen that both data sets are in a very good agreement with respect to short-term and long term variations.

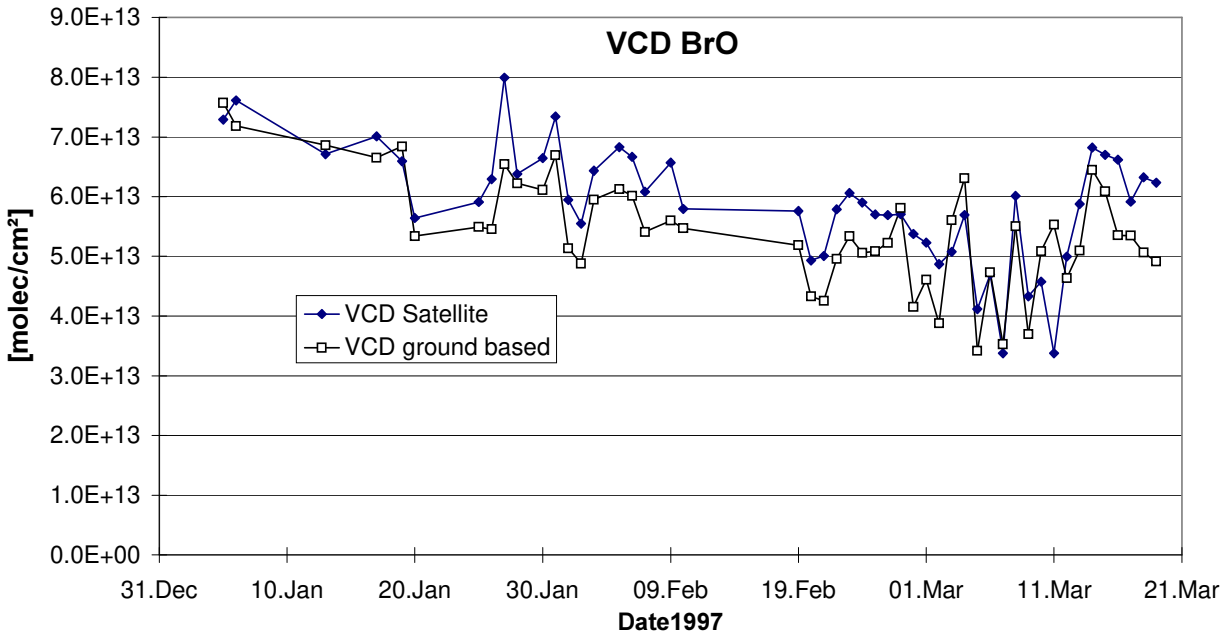


Figure 6.23 Comparison of the BrO VCD above Kiruna measured from ground and from satellite. For the calculation of the VCD from the SCD the AMFs for a profile height of 14 km (see appendix A) was used.

To investigate the influence of possible BrO concentrations in the free troposphere the impact of clouds on both data sets was studied.
An important aspect comparing ground based and satellite observations is that their fields of view are very different: While ground based observations typically use a very narrow field of view (1° for the observations at Kiruna) and thus observe a very small area of the sky, GOME observations cover a large area (typically 40 x 320 km, see section 3). Thus, while the sky above ground based instruments is either clear or cloudy, GOME measurements are almost always partly affected by clouds.
Thus it seems interesting to perform a selective comparison with respect to the cloud cover above the measuring site of the ground based instrument. The idea is that for GOME measurements a possible BrO concentration in the troposphere should be partly hidden by a partial cloud cover in nearly all measurements. In contrast, ground based observations are expected to be very sensitive to the local cloud cover (see Figure 5.16; Wagner et al., [1998e]).
There are two methods to decide whether the ground based measurements are affected by clouds. First, from satellite images the cloud cover over the measuring site can be determined. Second, the ground based observations also directly provide information about the local cloud cover from the measured intensities and the O_4 absorptions. This is illustrated in Figure 6.24, where satellite images of Scandinavia for two following days are shown [Dundee, 1999]. It can be seen that on March 4, 1997 the sky above Kiruna was clear while on the following day it was cloudy. This finding is also confirmed by the measurement of cloud-sensitive parameters from the ground (see e.g. Wagner et al., [1998]).

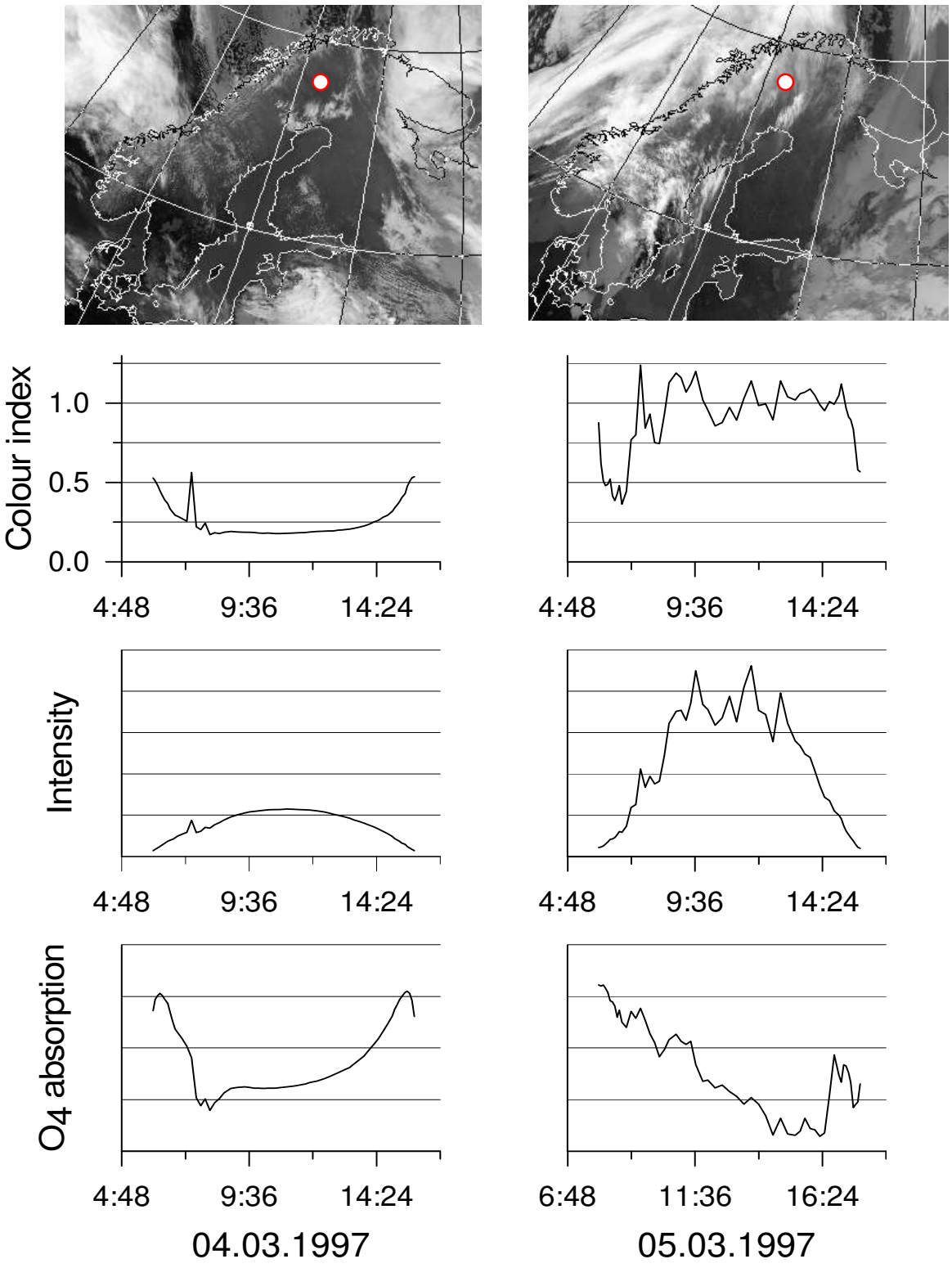


Figure 6.24 Determination of the cloud cover above Kiruna from satellite images and ground based observation of cloud-sensitive parameters. As indicated by the diurnal variation of the measured average intensity (380 to 680 nm), a colour index (ratio of the intensities at 670 and 388 nm) and the O_4 absorption, on 04.03.1997 the sky above Kiruna was clear (besides a small episode in the morning), on 05.03.1997 it was cloudy [Wagner et al., 1998e].

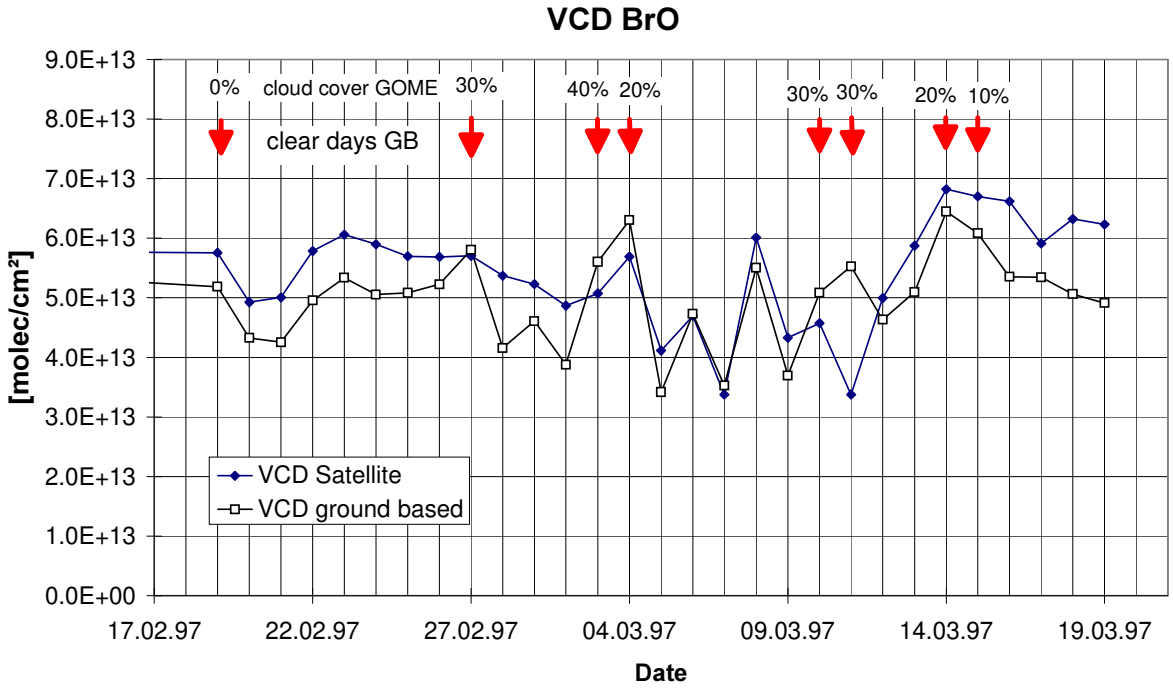


Figure 6.25 The same as Figure 6.23 but only for the second part of the period. During this part the SZA already reaches values < 80° at noon; for these SZAs it is useful to study the influence of clouds on the measurements. The days on which the sky was clear for the ground based measurements are indicated with arrows. The numbers above the arrows are the approximate cloud fractions for the GOME ground pixels used for the comparison. It is obvious that for the clear days the BrO VCDs show relatively high values compared to cloudy days. In particular for many of the clear days the BrO VCDs from the ground based measurements are larger than the BrO VCDs from the satellite observations. This effect is largest for days with relatively large cloud cover for the GOME ground pixels.

In Figure 6.25 the comparison between satellite and ground based measurements for part (mid February to mid March) of the whole period (Figure 6.23) is shown. This part was selected because the solar zenith angle during the GOME overpass was below about 80° for which the sensitivity to tropospheric species is higher than for larger SZA. It can be seen that for most of the cloud free days (with respect to the ground based measurements) BrO VCDs for both data sets are larger than for cloudy days. And in particular, for most of these days the BrO VCDs derived from the ground based instrument are systematically higher than for the satellite observation. This effect is largest for days with relatively large cloud cover for the GOME ground pixels.
These findings are consistent with the assumption that a large part of the total atmospheric BrO VCD is located in the free troposphere.

A new approach to derive the BrO absorption of the Fraunhofer spectrum from the comparison of ground based and satellite data

In contrast to satellite observations the Fraunhofer spectrum used for ground based DOAS measurements contains BrO absorption features, because no extraterrestrial spectrum measured with the same instrument is available. Usually, a spectrum measured at low SZA is used as Fraunhofer spectrum which contains only small atmospheric absorptions. However, to derive the

total SCD from the DOAS analysis, the BrO SCD of the Fraunhofer spectrum (SCD_{Ref}) has to be added to the retrieved difference in the SCDs of the measured spectrum and the Fraunhofer spectrum.
In appendix A we present a new method for the determination of SCD_{Ref}. Especially for species which are mainly located in the lower stratosphere and with a pronounced diurnal variation (like e.g. BrO and OClO) this method is more accurate than the methods normally used. This new method was in particular applied to the ground based BrO data presented in sections 6.4.1 and 6.4.3.

6.4.4 Summary of the GOME observations of BrO in the free troposphere

From several GOME observations indications have been presented in this PhD thesis that a significant part of the total atmospheric BrO column is located in the free troposphere. The results of these observations are summarised in Table 6.4.

Method	Latitudinal variation	Seasonal variation	Land/ocean dependence	Altitude dependence	BrO mixing ratio
Modelling of the pure stratospheric BrO SCDs (section 6.2)	no obvious dependence	strong variation	?	?	up to about 6 ppt
Comparison between GOME and ground based measurements (sections 6.4.1 and 6.4.2)	?	no obvious dependence	?	?	?
Comparison between GOME and balloon observations (section 6.4.2)	no obvious dependence	no obvious dependence	?	?	2.3 ppt for one case study
Influence of clouds on the GOME measurements (section 6.4.3)	no obvious dependence	no obvious dependence	higher mixing ratios above the ocean	in the Tropics probably located near the tropopause	up to 2 ppt in the Tropics

Table 6.4 Summary of the results of the different methods used to investigate possible BrO concentrations in the free troposphere. The BrO mixing ratios are derived from the BrO VCD assuming a constant mixing ratio in the troposphere. Question marks indicate that the respective methods can make no prediction.

In conclusion we state that it is very likely that BrO mixing ratios up to several ppt are present in the troposphere on a global scale. From the time series of the total BrO VCD measured by GOME there are indications of seasonal variation with a period of about one to two months. We also found indications of higher mixing ratios above the oceans compared to the continents. From observations over the Tropics it can be concluded that the main fraction of the tropospheric BrO is located in the upper troposphere. This is in good agreement with the results of a balloon sounding made at Bauru, 25° S [Pundt et al., 1999].