

## DOAS Zenith Sky Observations: 2. Seasonal Variation of BrO over Bremen (53°N) 1994–1995

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**Abstract.** Zenith sky observations of BrO over Bremen (53°N) are reported for the period of September 1994 to January 1996. BrO differential slant columns between 90° and 80° solar zenith angle showed a strong seasonal variation between a winter maximum of  $1.9 \cdot 10^{14}$  molec/cm<sup>2</sup> and a summer minimum of  $0.6 \cdot 10^{14}$  molec/cm<sup>2</sup>. The seasonal variation in BrO twilight values is shown to be inversely correlated with NO<sub>2</sub> columns in agreement with current knowledge of gas phase chemistry of bromine. In contrast to model predictions, no significant difference between morning and evening BrO measurements was observed. During a 6 day polar vortex excursion to mid-latitudes OClO could be measured above Bremen indicating chlorine activation in the vortex air. No significant increase in BrO differential slant columns was detected during this time.

**Keywords:** bromine oxide, OClO, stratosphere, mid-latitudes, remote sensing, UV absorption

### 1. Introduction

Anthropogenic emissions of chlorofluorocarbons and halon compounds are believed to be the primary cause of the springtime depletion of austral ozone and the potential cause of reduced ozone at high latitudes and mid-latitudes in the northern hemisphere (WMO, 1995, and references therein). Model calculations including homogeneous (Poulet *et al.*, 1992; Garcia and Solomon, 1994; Lary, 1996) and heterogeneous (Lary *et al.*, 1996) atmospheric bromine chemistry have demonstrated the ozone destruction potential of bromine compounds at northern high latitudes and, of particular interest for this study, at mid-latitudes. Bromine species are effective in destroying ozone both by BrO<sub>x</sub> catalytic cycles and by interactions which might accelerate loss by the HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> cycles.

In spite of their atmospheric significance, the number of field measurements of bromine compounds is still limited. BrO which is considered to be the dominant active bromine compound of the sunlit lower

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stratosphere has been measured in situ (Brune *et al.*, 1988; Brune *et al.*, 1989; Toohey *et al.*, 1990; Avallone *et al.*, 1995) and by UV spectroscopy (e.g. Carroll *et al.*, 1989; Perner *et al.*, 1991; Wahner *et al.*, 1990; Arpag *et al.*, 1994; Fish *et al.*, 1995; Eisinger *et al.*, 1997).

In this study, the first full year of zenith sky measurements of BrO is reported above Bremen (53°N). Simultaneously, measurements of O<sub>3</sub>, NO<sub>2</sub>, and OClO have also been acquired. The objective of this study is to take a first step towards establishing a climatology of BrO at mid-latitudes and to investigate any possible seasonal and diurnal variation of BrO. In addition, as the polar vortex came close to Bremen in January 1995, investigations of the BrO behaviour under vortex conditions were possible. The measurements were carried out from September 1994 to January 1996 as part of the SCUVS (Stratospheric Climatology using UV/Visible Spectroscopy) and SESAME (Second European Stratospheric Arctic and Mid-latitude Experiment) projects of the European Union. This continues a study of BrO above Bremen first described by Eisinger *et al.* (1997) for winter and early spring 1993 and 1994.

## 2. Experimental set-up and data analysis

### 2.1. EXPERIMENTAL

The measurements reported in this study were obtained using ground-based zenith sky scattered light spectroscopy. The experimental set-up is similar to that reported by Richter *et al.* (1995) and Eisinger *et al.* (1997). In brief, light scattered in the zenith is collected by a small telescope and is then directed to a temperature stabilised 500 mm Czerny Turner spectrograph with a 1024 pixel Reticon diode-array detector. The spectral resolution of the instrument was 0.5 nm FWHM before 15 January 1995 when it was changed to 1.0 nm by increasing the slit width from 50 to 100  $\mu\text{m}$ . The spectral range observed by the instrument was 320 to 500 nm. A second instrument with a spectral resolution of 1.4 nm was operated simultaneously in the wavelength region of 400 to 700 nm and was used for the determination of O<sub>3</sub> and NO<sub>2</sub> vertical columns (Richter *et al.*, 1995). Spectra of the light scattered from the zenith sky were recorded continuously. To optimise the signal to noise ratio of the spectra, the integration time of the diode array was adjusted automatically. After subtraction of dark signals and wavelength calibration the measurements were averaged over intervals of 600s.

Table I. Comparison of the fit results for 1995 using the (S) standard evaluation (one ozone absorption cross section at 220 K) and (O) the modified evaluation using the slant optical depths. The first two rows contain the BrO DSCDs in units of  $10^{14}$  molec/cm<sup>2</sup>. The last row (R) contains the ratio of the rms values of the fit residuals (standard / modified). For the standard evaluation the rms of the summer fits was so large, that BrO retrieval was not possible.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
S	1.89	1.53	1.12	0.61	0.82				0.61	0.93	1.62	2.23
O	1.90	1.50	1.17	0.75	0.79	0.67	0.59	0.65	0.65	0.92	1.35	1.95
R	1.10	1.02	1.10	1.42	1.69	2.31	2.30	1.90	1.39	1.14	1.07	1.12

## 2.2. DATA ANALYSIS

The spectra were analysed using a modified Differential Optical Absorption Spectroscopy (DOAS) technique. In this analysis, slant columns of atmospheric absorbers are determined by a linear fit of their differential absorption cross sections to the difference in optical depth of two zenith sky spectra obtained at different solar zenith angles. A low order polynomial is included in the fit to account for the wavelength dependence of Mie and Rayleigh scattering and the broad band absorptions of the trace gases. The filling in of Fraunhofer lines by rotational Raman scattering is accounted for by fitting an empirical Ring spectrum which was obtained in a manner described by Solomon *et al.* (1987). A theoretical Ring spectrum which was calculated assuming rotational Raman scattering as the main cause for the Ring effect was found to be in good agreement with the empirical spectrum (Burrows *et al.*, 1995). In order to compensate small changes in the wavelength calibration of the instrument, the sky spectra and the cross sections are allowed to vary their wavelength axis in the fit by a nonlinear shifting and stretching procedure (Richter, 1997). The relative alignment of the absorption cross sections, however, remains fixed.

In the UV wavelength range, this approach has been optimised by replacing the ozone cross sections with the *slant optical depth* of ozone as computed by the radiation transfer model GOMETRAN (Rozanov *et al.*, 1997). For a number of solar zenith angles the scattered intensity with and without ozone have been computed; the logarithm of the ratio was then used in the fit in place of the absorption cross section of ozone. It is important to note, that the ozone column still is derived by the fit, only vertical profile shape of ozone densities and temperature are assumed from the climatology.

This procedure has the advantage that the wavelength dependence of the airmass factor and the temperature dependence of the ozone absorption cross section in the Hartley-Huggins bands is accounted for correctly, which results in smaller fit residuals and a lower detection limit. This is illustrated in table I, where the results of the improved analysis are compared to those of the standard analysis using one ozone cross section at 220 K. A different set of slant optical depths has been computed for each month using the MPI climatology of pressure, temperature and ozone profiles provided by Brühl and Crutzen (1992). This strategy reduces any possible effect of the seasonal variations in atmospheric conditions (i.e. the temperature dependence of the ozone absorption cross sections) on the retrieved slant columns. Compared to the results of the standard analysis the differential slant columns of BrO are somewhat decreased in winter while the rms of the residuals is improved allowing BrO detection during the summer months which was not possible with the standard approach (see table I). On the other hand, when the measurements are analysed using summer slant optical depths for winter measurements and vice-versa, the quality of the fit is deteriorated: the residuals are larger by a factor of 2 – 3, BrO is below the detection limit in summer and winter BrO values are increased by up to 10 % when compared to the standard analysis. In summary, the “optimised” analysis procedure significantly improves the rms of the fit and makes summer time detection of BrO above Bremen possible. The seasonal variation of the BrO DSCDs which is discussed in section 3 is clearly observed in the results from both the standard and the modified analysis (see table I).

The relative absorption cross sections of NO<sub>2</sub> have been measured with the field instrument at 220K and were scaled to the absolute values of Harwood and Jones (1994). The spectra of BrO and OClO have also been measured in this laboratory, and for the relative shape good agreement with the values of Wahner *et al.* (1988) and Wahner *et al.* (1987) has been found. To facilitate comparison with previous measurements, in this work the absorption cross sections of Wahner *et al.* were used after convolution to the resolution of the Bremen instrument. For the O<sub>4</sub> absorption cross sections the values of Greenblatt *et al.* (1990) were used.

Differential BrO Slant Columns (DSCDs) were computed from the wavelength window 344.7 to 359.0 nm using a background spectrum taken at 80° SZA during the same twilight. From the residuals of the fit, the detection limit for BrO is estimated to be  $5 \cdot 10^{13}$  molec/cm<sup>2</sup>. The resulting DSCDs were then averaged for all measurements with

zenith angles in the range of  $88^\circ$  to  $91^\circ$ . Only DSCDs having linear fit errors less than 25% were included in the average; the total errors of the BrO DSCDs including the uncertainties of the absorption cross sections are estimated to be 30-40%. Details about the window selection and an error discussion can be found in Eisinger *et al.* (1997) and will not be repeated here.

One BrO absorption band (at 354.7 nm) coincides with a NO<sub>2</sub> absorption feature; thus a spectral interference could result in a correlation of the retrieved values of the two absorbers. Such a correlation should be visible in day-to-day variations, seasonal variations and during NO<sub>2</sub> pollution periods. In fact, NO<sub>2</sub> slant columns show a seasonal *anti*-correlation with BrO DSCDs, and no (anti-)correlation in the day-to-day variations or during pollution events (see section 3). Possible interference of the temperature dependence of the NO<sub>2</sub> absorption cross section has been tested by using NO<sub>2</sub> measured at 240K, 273K and 293K in the analysis. For all temperatures, the resulting BrO DSCDs differ by no more than 6% from the values obtained with the 220K absorption cross sections. From this it is concluded, that spectral interference of NO<sub>2</sub> does not introduce significant errors into the BrO DSCDs.

For BrO, the conversion of the measured differential slant columns to vertical columns is difficult because of the uncertainties in the vertical profile and the large horizontal gradients which arise from the photochemical conversion of bromine compounds during twilight. Therefore only differential slant columns derived in the manner described above are discussed.

### 3. Results

In this work, 17 months of continuous zenith sky measurements of BrO above Bremen are reported for 1994, 1995 and early 1996. These measurements cover a wide range of different atmospheric conditions thus facilitating the study of the influence of season, NO<sub>2</sub> columns, and air mass origin on the BrO DSCDs measured at mid-latitudes.

In figure 3 BrO AM DSCDs are shown for the period of September 1994 to January 1996. Both a large day to day variability and a strong seasonal variation with a pronounced winter maximum of  $1.9 \cdot 10^{14}$  molec/cm<sup>2</sup> were observed. Absolute day to day variations were largest during winter and spring, when BrO DSCDs were large, and much smaller in summer. BrO slant columns measured in summer were sometimes as small as  $5 \cdot 10^{13}$  molec/cm<sup>2</sup> which is the estimated

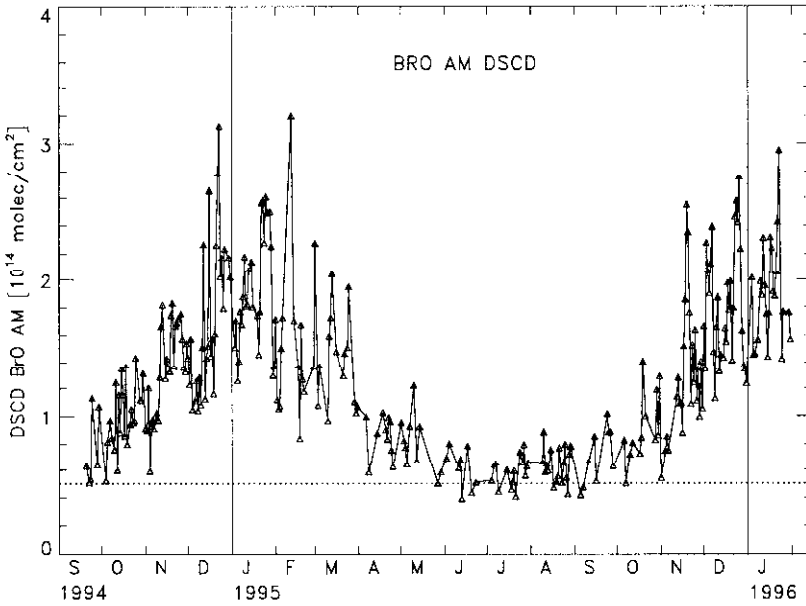


Figure 1. BrO AM DSCDs ( $60^{\circ}$ – $80^{\circ}$  SZA) above Bremen. The dotted line is the estimated detection limit.

detection limit of the experiment. Thus for these days only an upper limit of  $5 \cdot 10^{13}$  molec./cm<sup>2</sup> can be given for BrO.

In figure 3 monthly averages of BrO DSCDs are shown for both AM and PM measurements. The seasonal variation appears to be similar for the two winters covered by the measurements. Morning and evening twilight measurements show no significant difference within the errors of the measurements. This is also true for the variation of BrO DSCD with SZA which is smooth and similar for AM and PM measurements as shown in figure 3 for June and December 1995.

In figure 3 morning and evening DSCDs of NO<sub>2</sub> are shown. Measurements with large tropospheric perturbations have been removed after examination of the NO<sub>2</sub> and O<sub>4</sub> Langley-plots, resulting in DSCDs which are dominated by stratospheric NO<sub>2</sub>. Comparison with figure 3 reveals a strong anti-correlation between the seasonal variation of BrO and NO<sub>2</sub> DSCDs. This relationship is further illustrated in figure 3. While day to day variations are not correlated, the seasonal behaviour of BrO and NO<sub>2</sub> clearly is. It is interesting to note, that episodes with large NO<sub>2</sub> slant columns due to tropospheric pollution (not shown in the plots) do not correspond to particularly small (or large) BrO slant columns. From the above it is concluded that the observed anti-

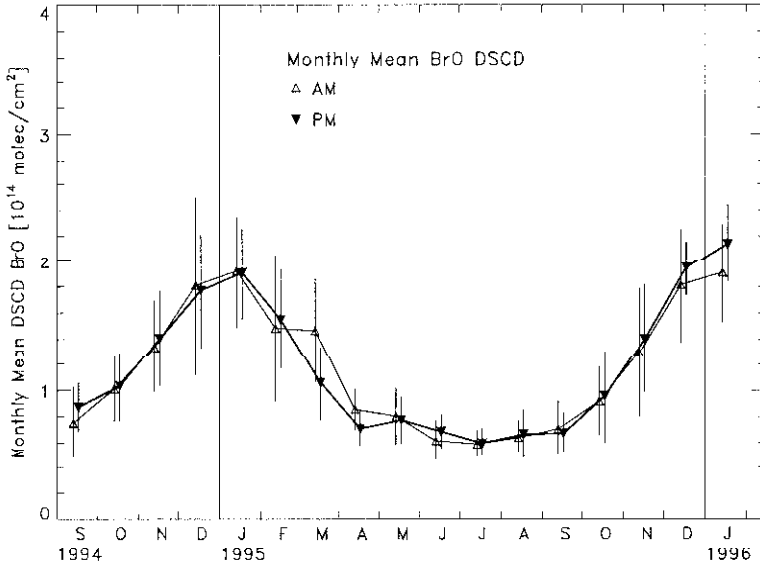


Figure 2. Monthly means of BrO AM and PM DSCDs. Open triangles denote AM, filled triangles PM measurements. The bars indicate the  $1\sigma$  standard deviation of the average.

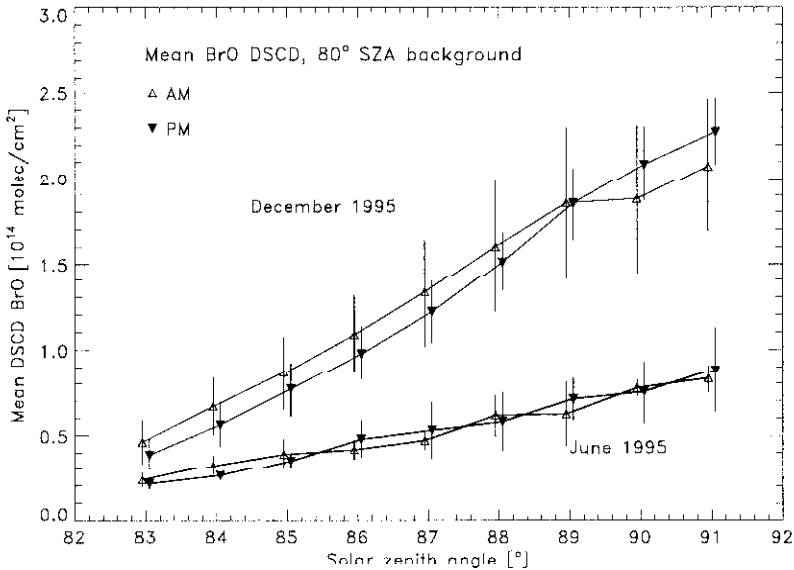


Figure 3. Monthly averaged DSCDs for June and December 1995. Open triangles denote AM, filled triangles PM measurements. The bars indicate the  $1\sigma$  standard deviation of the average.

correlation is real and has to be explained by a direct or indirect interaction of stratospheric BrO and NO<sub>2</sub>.

NO<sub>2</sub> DSCDs are correlated with stratospheric temperatures at 50 hPa (see figure 3). Similar correlations have been observed both in Antarctic (Mount *et al.*, 1987) and Arctic measurements (Pommereau and Goutail, 1988; Goutail *et al.*, 1994). These authors ascribe the observation to the temperature dependence and photolysis of the main NO<sub>2</sub> reservoir N<sub>2</sub>O<sub>5</sub>. Mount *et al.* consider that gas phase chemistry alone can not explain the correlation, and that PSCs and dynamics may play a part. Above Bremen at 53°N, the most likely explanation of the NO<sub>2</sub> – T correlation is the change in length of day, which in summer results in more photolysis and thermal decomposition of the NO<sub>2</sub> precursors, and at the same time higher temperatures.

## 4. Discussion

### 4.1. SEASONAL VARIATION OF BRO AND CORRELATION WITH NO<sub>2</sub>

In two previous studies from other groups the seasonal variation of stratospheric BrO has been addressed: zenith sky measurements above Colorado (40°N) by Arpag *et al.* (1994) and in situ measurements by Avallone *et al.* (1995). Eisinger *et al.* discussed the winter and spring behaviour of BrO in 1993 and 1994.

Arpag *et al.* reported DSCDs of BrO for the period from January 22 to May 24, 1993. The measurement set-up of that study differs from the one used in this work in its viewing geometry. The telescope was initially pointed at an 80° angle relative to the zenith towards the setting sun and was re-orientated towards the east on April 17. In contrast to the results presented in this study, no seasonal variation was observed in their measurements.

Eisinger *et al.* discussed the winter and spring BrO measurements above Bremen in 1993 and 1994. While no seasonal variation could be derived from that data set alone, the December maximum and the decrease during spring is similar to the variations observed in the next two winters.

Avallone *et al.* reported average values of BrO mixing ratios measured from the NASA ER-2 on a number of flights in February and October. Both before and after the eruption of Pinatubo, the October measurements showed smaller values at northern mid-latitudes. While a comparison of the in situ measurements with the BrO DSCDs reported in this work is not simple, it is worthwhile to note, that they reported a ratio of 1.3 – 1.5 between February and October measurements which



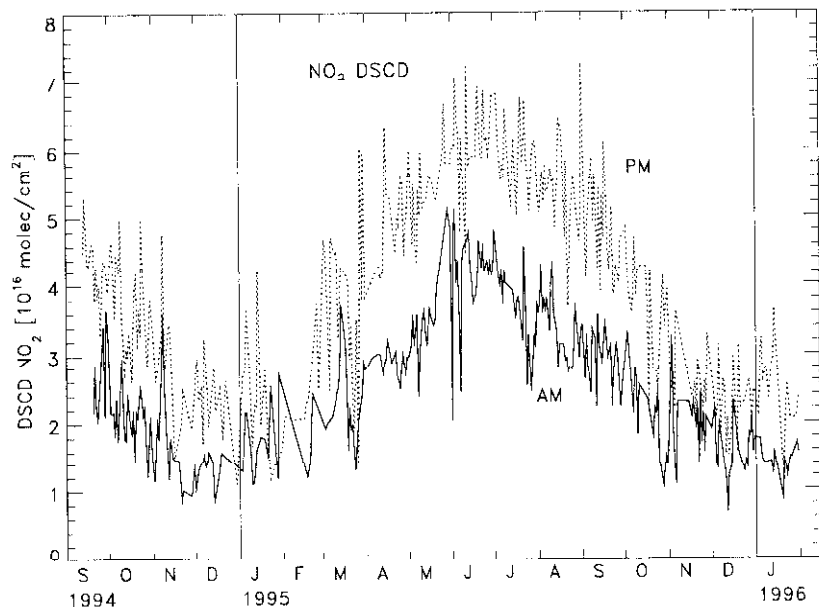


Figure 4.  $\text{NO}_2$  AM and PM (dashed line) DSCDs ( $90^\circ$ - $80^\circ$  SZA) above Bremen. Measurements with large tropospheric perturbations have been removed.

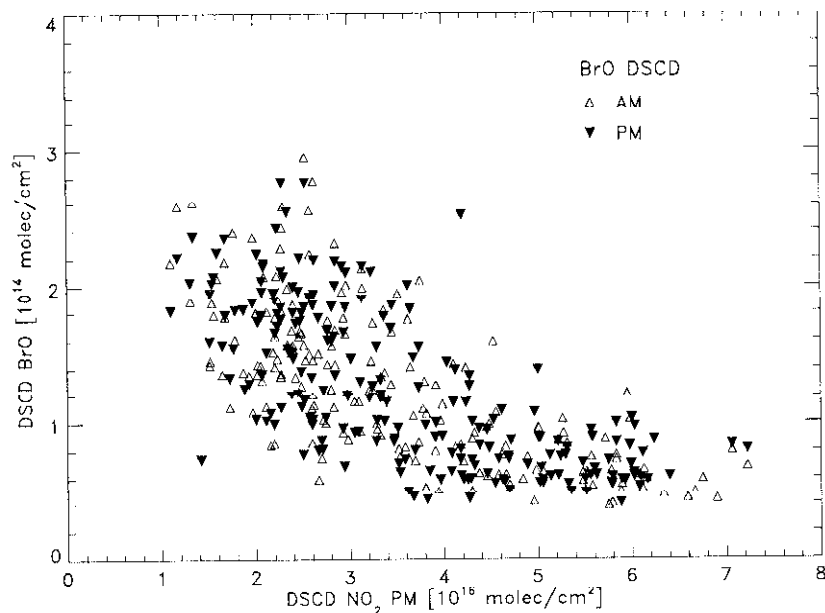


Figure 5. Scatter plot of BrO and  $\text{NO}_2$  DSCDs. Open triangles denote BrO AM, filled triangles BrO PM measurements. Note that not all BrO DSCDs are included in this plot because of the selection criteria applied to the  $\text{NO}_2$  values.

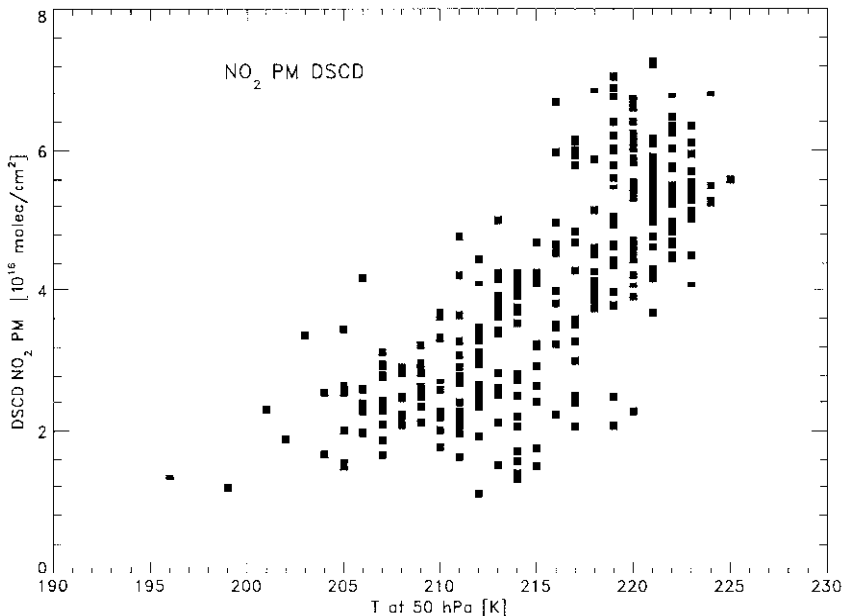


Figure 6. Scatter plot of  $\text{NO}_2$  evening DSCDs and 50 hPa ECMWF temperatures.

is in excellent agreement with the variation of approximately 1.5 which can be inferred from figure 3.

A marked seasonal variation of BrO has been predicted from model calculations (Fish *et al.*, 1995; Danilin and McConnell, 1995) and is explained by the rapid response of  $\text{BrONO}_2$  and BrO concentrations to changes in  $\text{NO}_2$ . An increase in  $\text{NO}_2$  concentration leads to an increase of  $\text{BrONO}_2$  and a corresponding decrease of BrO. This relation still holds if in a second step  $\text{BrONO}_2$  is converted to HOBr by heterogeneous hydrolysis on sulphate aerosols.

Thus BrO and  $\text{NO}_2$  concentrations should be inversely correlated, which is consistent with the measurements as shown in figure 3. Together with the seasonal variation of  $\text{NO}_2$ , this yields a qualitative explanation of the observed seasonal variation of BrO DSCDs. As previously mentioned, the day to day variations of BrO and  $\text{NO}_2$  show no correlation. Several factors can contribute to this observation:

- the fit error of the BrO DSCDs;

the uncertainty in the tropospheric contribution of the total  $\text{NO}_2$  column amount;

- zenith sky measurements of  $\text{NO}_2$  are weighted towards the maximum of  $\text{NO}_2$  which varies in the range 20 – 35 km while BrO is thought to reside mainly between 15 – 20 km (Fish *et al.*).

Thus day-to-day variations of the  $\text{NO}_2$  DSCDs are not necessarily determined by  $\text{NO}_2$  behaviour at the height of the BrO maximum. In contrast seasonal changes of  $\text{NO}_2$  are dominated by the change in day length and therefore are expected at all altitudes, providing a simple explanation of the observed BrO DSCD behaviour.

This is the first time that a BrO anti-correlation with  $\text{NO}_2$  has been observed. In contrast, both Arpag *et al.* and Fish *et al.* explicitly report that their  $\text{NO}_2$  DSCDs were *not* correlated with BrO DSCDs. In the study of Fish *et al.* any correlation may well be masked as a result of the limited number of data points and possibly tropospheric  $\text{NO}_2$  pollution. The measurements of Arpag *et al.* covered several months and a substantial range of  $\text{NO}_2$  columns at 40° N. There are several differences between the measurements at 40°N and those in this study, which are relevant to possible BrO /  $\text{NO}_2$  correlations:

- the seasonal variation in  $\text{NO}_2$  is much larger at 53°N;
- as the polar vortex is often displaced towards Northern Europe, the influence of cold,  $\text{NO}_2$  low air is likely to be more important above Bremen than above Colorado;
- stratospheric aerosol loading was much larger in 1993 than in 1995 and may have influenced the BrO –  $\text{NO}_2$  anti-correlation by heterogeneous conversion of  $\text{BrONO}_2$  to HOBr and possibly to BrCl dependent on temperature (Lary *et al.*, 1996).

The only other simple explanation of the BrO behaviour would be a seasonal variation of stratospheric  $\text{Br}_y$ . However, we are not aware of any theoretical or observational study which predicts such a seasonal variation of  $\text{Br}_y$  at mid-latitudes.

BrO will also vary with changes in stratospheric temperatures. The negative temperature dependence of the formation of  $\text{BrONO}_2$  results in larger concentrations of BrO during summer. Using the temperature dependence recommended by DeMore *et al.*, 1994 the rate constant decreases by a factor of 1.4 when temperature changes from 200 to 225 K. This increase of BrO concentrations with temperature is not observed in the measurements and is probably overcompensated by loss from the large increase in  $\text{NO}_2$ .

An additional but smaller effect is the influence of stratospheric temperature changes on the absorption cross sections of  $\text{NO}_2$  and BrO. Differential  $\text{NO}_2$  absorption cross sections in the selected wavelength

region decrease by approximately 0.15% for a temperature increase of 1 K (Dehn, 1995) while BrO absorptions decrease by approximately 0.5% per K. The latter assumes a linear extrapolation of the T-dependance of the BrO absorption cross sections measured by Wahner *et al.* (1988). Thus BrO slant columns may be overestimated at low temperatures by up to 15%, NO<sub>2</sub> slant columns by up to 5%. Clearly, both effects can only explain a small part of the variations in figure 3. However in order to improve the accuracy of the BrO DSCDs, an improved knowledge of the temperature dependence of the absorption cross section of BrO has to be established.

In summary, the observed seasonal variation of BrO DSCDs is consistent with BrO concentrations being controlled by stratospheric NO<sub>2</sub>. This result is similar to the inverse correlation of ClO and NO<sub>2</sub> reported by Stimpfle *et al.*, 1994 from in situ measurements.

#### 4.2. DIURNAL VARIATION OF BRO

From the monthly averaged DSCDs shown in figure 3 no significant difference in morning and evening values can be deduced. The same result is obtained from the examination of the diurnal variation of BrO DSCDs integrated over 1° SZA intervals which is shown in figure 3 for June and December 1995: while measurements on individual days show both smaller and larger AM values, the average DSCDs differ by no more than  $2 \cdot 10^{13}$  molec/cm<sup>2</sup>.

Fish *et al.* observed differences in sunrise and sunset DSCDs, which increase from  $2 \cdot 10^{13}$  molec/cm<sup>2</sup> at 88° SZA to  $1 \cdot 10^{14}$  molec/cm<sup>2</sup> at 91°. Model calculations of Fish *et al.* and Chipperfield *et al.* predict an even larger difference in dawn and dusk DSCDs because BrONO<sub>2</sub> and HOBr as the major bromine nighttime reservoirs have a long lifetime at large solar zenith angles and therefore BrO is not in photochemical steady state during sunrise.

One possible explanation of the model underestimation of morning BrO DSCDs is the use of low values for the absorption cross sections of BrONO<sub>2</sub> and HOBr. As pointed out by Chipperfield *et al.* there is a considerable spread in literature values, and recent measurements (Burkholder *et al.*, 1995; Deters *et al.*, 1996a, 1996b; Rattigan *et al.*, 1996) all indicate larger absorption cross sections for the bromine reservoirs than those used in current models. Larger absorption cross sections lead to higher photolysis frequencies (shorter photolytic lifetimes) and accelerate the morning release of BrO. It is therefore to be expected that incorporation of the improved absorption cross sections into the models will reduce the predicted difference and thus improve the agreement between model calculations and measurements.

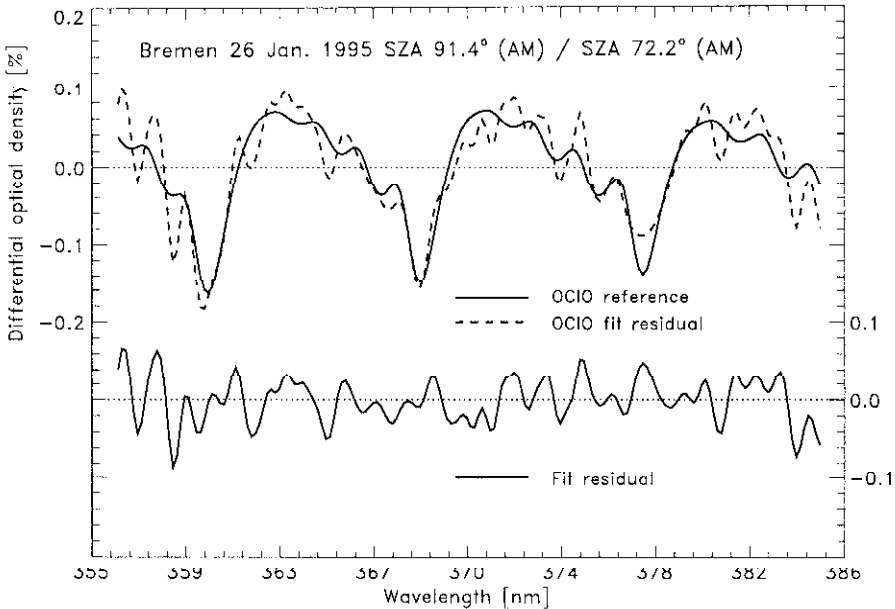


Figure 7. OCIO fit results for 26 January 1995, 91.43° SZA AM. The bold line is the laboratory reference, the dashed line the fit result. The curve at the bottom is the residual of the fit.

In summary, no significant difference between morning and evening BrO DSCDs could be observed in 1994 and 1995. This is consistent with the measurements of Eisinger *et al.* but in contradiction to the model results of Fish *et al.*

#### 4.3. BRO AND OCLO IN VORTEX AIR

In January 1995, the edge of the polar vortex reached Bremen for a 6 day period. It is of interest to note, that it was only on these few days out of the entire 17 months measurement set that OCIO DSCDs were above the estimated detection limit of  $0.7 \cdot 10^{14}$  molec/cm<sup>2</sup>.

An example of the fit results is given in figure 4.2. OCIO DSCDs at 90° SZA using a reference spectrum taken at noon (71.9° SZA) are in the range of  $1.1 - 1.7 \cdot 10^{14}$  molec/cm<sup>2</sup>. These large values are a strong indication of chlorine activation in the vortex air. In figure 4.3 the OCIO DSCDs are shown together with the respective BrO values. The potential vorticity at the 435 K level is also included to identify the vortex period. BrO DSCDs were already large above Bremen during this time of the year, and in contrast to OCIO there was no significant enhancement during the overpass of vortex air. It is therefore

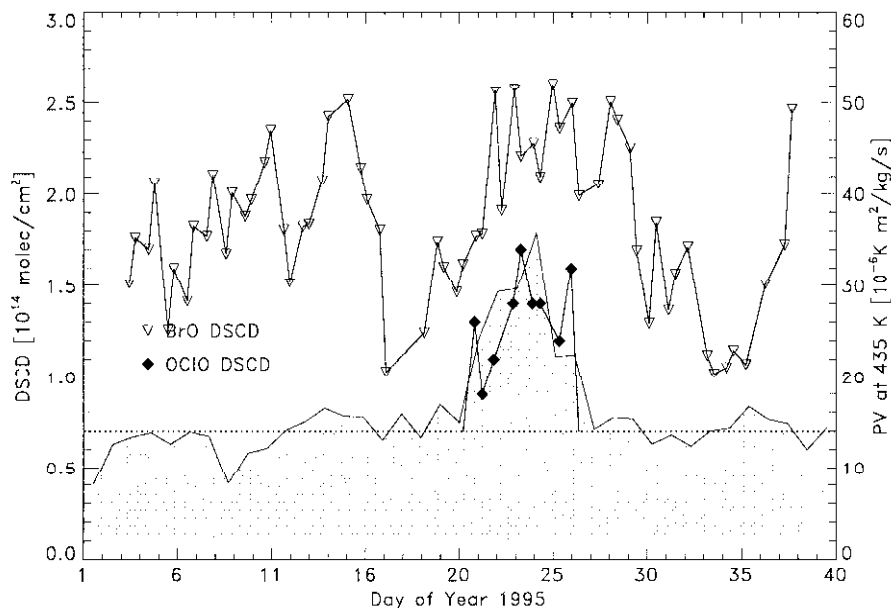


Figure 8. DSCDs of BrO (open triangles) and OCIO (filled diamonds) for January and February 1995. Both AM and PM values are included. The shaded area indicates the ECMWF potential vorticity at 435 K, the dotted line is the estimated detection limit for OCIO.

concluded, that bromine partitioning was not significantly different in polar and mid-latitude air at that time.

This result is in contrast to the findings of Brune *et al.* (1989) and Toohy *et al.* who report enhanced BrO concentrations from in situ measurements in both Antarctic and Arctic vortex air. However, the measurements in this investigation are in agreement with the results of Avallone *et al.* who observed no significant difference in BrO/Br<sub>y</sub> within the polar vortex relative to that at mid-latitudes and presented measurements of BrO which yield similar concentrations in both vortex and non-vortex air.

In conclusion large OCIO modulation but no significant BrO variation was observed between vortex and non vortex air above Bremen in January 1995.

## 5. Summary

In this study, 17 months of continuous zenith sky observations of BrO have been reported for 1994 – 1996. BrO DSCDs showed a marked

seasonal variation with a maximum in winter. The annual cycle was inversely correlated with that of NO<sub>2</sub> DSCDs which is consistent with the control of twilight BrO concentrations by the gas phase formation and photodissociation of BrONO<sub>2</sub>. The seasonal variation of NO<sub>2</sub> then explains best the observed seasonal variation in BrO DSCDs. Both the seasonal variation and the anti-correlation with NO<sub>2</sub> are in contrast to previous zenith sky measurements (Arpag *et al.*, 1994), but in agreement with in situ measurements (Avallone *et al.*, 1995) and model predictions (Fish *et al.*, 1995).

No significant difference between morning and evening BrO values can be deduced from the data. This is at odds with model predictions and is possibly explained by the use of low absorption cross sections of BrONO<sub>2</sub> and HOBr in the models.

In January 1995, the stratosphere above Bremen was within the polar vortex for a period of 6 days. Only during this period was OCIO detected, indicating chlorine activation in the vortex air. In contrast to OCIO, BrO DSCDs were not significantly different inside and outside the vortex. This is further indication that for BrO differences between the vortex and mid-latitude chemistry are much smaller than for chlorine.

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