

DOAS Zenith Sky Observations: 1. BrO Measurements over Bremen (53° N) 1993–1994

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(Received: 10 October 1996)

Abstract. Observations of stratospheric BrO over Bremen (53° N) are reported for winter and early spring periods of 1993 and 1993/94. The BrO was observed by ground-based near-UV absorption spectroscopy of sunlight scattered in the zenith. Differential slant column densities for solar zenith angles 90°/80° in the range of 9×10^{13} (detection limit) to 4.5×10^{14} molecules/cm² having a high day-to-day variability were found. For the majority of the measurements no significant difference was observed between the morning and evening behaviour of BrO. Exceptions are the morning measurements from the winter of 1992/93 where an accelerated production of BrO was observed. We believe the latter best to be explained by the early morning rapid photolysis of elevated amounts of photo-labile Br-reservoirs formed during the night. The largest differential slant column densities of BrO were measured in December 1993 when the temperatures at 30 hPa dropped below 205 K. This might be an indication of heterogeneous conversion of bromine compounds on sulfate and other aerosols.

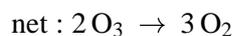
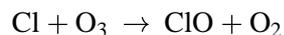
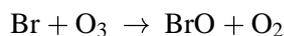
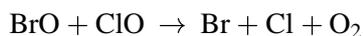
Key words: bromine oxide, stratosphere, midlatitudes, remote sensing, UV absorption.

1. Introduction

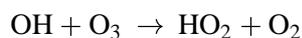
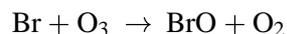
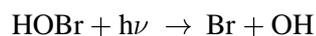
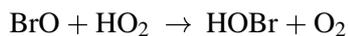
Catalytic cycles involving bromine compounds have been recognized for some time to be a potentially important mechanism for stratospheric ozone depletion (Wofsy *et al.*, 1975; Yung *et al.*, 1980). In the stratosphere bromine is released by photolysis and OH/O(¹D) oxidation of its tropospheric source gases methyl bromide and the halons. Currently mixing ratios of total available inorganic bromine Br_y are estimated to be in the range of 10–25 pptv in the lower stratosphere. In spite of its lower abundance compared to 3.2 ppbv of total chlorine, the bromine cycles can be very effective in removing ozone because the potential reservoirs Br₂, BrCl, BrONO₂, and HOBr are rapidly photolysed in the sunlit atmosphere. As a direct result, a large fraction of the daytime Br_y exists in reactive forms BrO_x, the majority being BrO (Lary, 1996).

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A catalytic reaction cycle coupling chlorine and bromine (McElroy *et al.*, 1986)



is believed to account for 15–30 % of the ozone loss in polar spring where ClO concentrations are elevated, and those of NO_x suppressed as a result of heterogeneous processing (Anderson *et al.*, 1989), while a coupled hydrogen-bromine cycle



is important at midlatitudes and is independent of any Cl interaction. The second cycle has its strongest impact on the lowest part on the stratosphere (Poulet *et al.*, 1992; Garcia and Solomon, 1994). The BrO_x and NO_x species are linked via formation and photolysis of BrONO₂. Heterogeneous processes, such as hydrolysis of N₂O₅, ClONO₂, and BrONO₂ on sulfate aerosols, enhance halogen activation.

In spite of their importance in the chemistry of the stratosphere, the number of field measurements of bromine containing constituents is limited. This results both from their relatively low concentrations and the difficulty of accessing the stratosphere. For the minor bromine reservoir HBr, stratospheric mixing ratios between 1.6 and 2.0 pptv have been determined by far-infrared emission spectroscopy (Johnson *et al.*, 1995; Carlotti *et al.*, 1995). Although stable Br sources such as CH₃Br or the halons can be measured by grab sampling and subsequent gas chromatographic or mass spectroscopic analysis, the reactive gases must be measured by either *in situ* or remote sensing techniques. BrO was first detected in the stratosphere above Antarctica by ground-based UV spectroscopy similar to that used in this study (Solomon *et al.*, 1989; Carroll *et al.*, 1989). In the northern hemispheric polar regions both ground-based (Perner *et al.*, 1991) and airborne (Wahner *et al.*, 1990; Wahner and Schiller, 1992) measurements have been successfully made by similar techniques. BrO mixing ratios have been determined *in situ* over Antarctica (Brune *et al.*, 1989), the Arctic (Toohey *et al.*, 1990; Avallone *et al.*, 1995), and midlatitudes (Brune *et al.*, 1988; Avallone *et al.*, 1995). Recently measurements of BrO at midlatitudes have been reported using ground-based remote sensing (Arpag *et al.*, 1994; Fish *et al.*, 1995).

Monitoring bromine chemistry is essential for a quantitative understanding of the observed mid-latitude lower stratosphere ozone losses. In this study ground-based BrO observations above Bremen (53.1° N, 8.9° E) are reported. The measurements were carried out from January to April 1993, and from October 1993,

to April 1994, as part of the European SCUVS (Stratospheric Climatology using UV/Visible Spectroscopy) and SESAME (Second European Stratospheric Arctic and Mid-latitude Experiment) projects.

2. Observations

The technique used to observe the BrO utilizes the spectroscopy of zenith scattered sunlight from the ground. This approach to passive remote sensing of atmospheric constituents was pioneered by Brewer *et al.* (1973), Noxon *et al.* (1975, 1979), and Solomon *et al.* (1987).

2.1. EXPERIMENTAL SETUP

The experimental setup in Bremen has been described elsewhere (Richter *et al.*, 1995). In brief, sunlight scattered from the zenith sky is focussed onto a quartz fibre which directs it to the entrance slit of a Czerny–Turner spectrograph ($f = 500$ mm) operating in the wavelength region 322–485 nm and having a spectral resolution of 0.5 nm (FWHM). Zenith sky spectra are recorded whenever the solar zenith angle (SZA) is less than 96° by a Reticon photodiode array (electronics: EG&G Mod. 1412) cooled to -40°C . In order to spectrally calibrate the zenith sky spectra, the output of a mercury-cadmium lamp is recorded regularly.

2.2. DATA ANALYSIS AND ERROR DISCUSSION

After dark signal correction and wavelength calibration zenith sky spectra are averaged over 10-minute intervals and evaluated using the method which has become known as differential optical absorption spectroscopy (DOAS). The first step in this approach is to divide a spectrum $I(\lambda)$ taken at some given SZA by a background spectrum $I_B(\lambda)$ having a shorter path through the atmosphere. In this study either the noon spectrum or that at SZA 80° was chosen as the background. The change in atmospheric optical density is given by

$$D(\lambda) = \ln \frac{I_B(\lambda)}{I(\lambda)}.$$

In a nonlinear least-squares fit differential reference spectra of O_3 , NO_2 , BrO, an empirical Ring spectrum and a second order polynomial for removing the contributions of Rayleigh and Mie scattering are fitted simultaneously to D , yielding the change in slant column density between the two measurements, or the differential slant column density (DSCD) for each absorber.

The relative absorption cross sections of O_3 and NO_2 have been measured in the laboratory with the field instrument at temperatures between 210 and 220 K. They have been scaled to the absolute values of Bass and Paur (1985) and Harwood and Jones (1994). The Ring spectrum was also measured with the field instrument, using the polarizer method described by Solomon *et al.* (1987). The BrO spectrum

has been taken from Wahner *et al.* (1988), which is in agreement with spectra recorded in this laboratory. It has been convolved to the resolution of the Bremen instrument.

The choice of the wavelength region for spectral analysis is of critical importance for the detection of weak atmospheric absorbers such as BrO, having differential absorbances of the order of 10^{-3} . Below 345 nm BrO absorptions are strongly masked by absorption of the ozone Huggins bands. The (6,0) absorption band of BrO at 344 nm coincides with an ozone feature and with the Fraunhofer O line and therefore is excluded from the fitting region. The weak (3,0) band at 360.4 nm is disturbed by interference from O₄. Only the (5,0) band at 348.8 nm and the (4,0) band at 354.7 nm are relatively free for analysis. The same two bands have been used in previous studies (Carroll *et al.*, 1989; Wahner *et al.*; 1990; Perner *et al.*, 1991; Arpag *et al.*, 1994; Fish *et al.*, 1995). Nevertheless the (4,0) band has an interference from an absorption feature of NO₂. Therefore, the exact wavelength region containing the two selected BrO bands has been optimized to minimize both (i) BrO linear fit errors and (ii) spectral interference between BrO and NO₂. The latter was achieved by including another NO₂ feature (357.4 nm) which does not correlate with BrO absorption. The wavelength region from 344.7 to 359.0 nm was found to be the most suitable for the analysis. After significant testing, spectral correlation between BrO and NO₂ leading to an artifact in measured BrO DSCDs has been ruled out.

For the study of the day-to-day variations of BrO and for comparison with other relevant measurements, DSCDs are calculated between 80° and 90° SZA, by using the 80° spectra as background and linearly interpolating the 90° DSCD between adjacent measurements. At 53° N this corresponds to a time interval of one hour (at the equinox) to two hours (at the winter solstice) between the two measurements. At these large SZAs, measurements are weighted heavily towards stratospheric absorbers. The DSCD values of BrO are therefore interpreted as stratospheric BrO values. Further detailed investigations are required to quantify the error on the stratospheric BrO DSCD values induced by the presence of small amounts of tropospheric BrO.

The total error of the BrO DSCDs is dominated by errors in the reference spectra of the strong absorbers O₃ and NO₂. Of particular importance are the temperature dependences of these spectra, which are well established for the Huggins bands of ozone and still disputed for NO₂. For the fitting procedure a single temperature has to be chosen for each reference although the atmosphere covers a broad temperature range. Spectral correlation between the trace gases included in the fit also contributes to the total error. A minor but not negligible part of the error is caused by mismatches in spectral resolution between trace gas references and zenith sky spectra. From results of several fits with different parameters the total error of the DSCDs is estimated to be 30–40 %.

To be distinguished from the total error is the error of the linear fit which tells only about the quality of the fit. In the following only BrO values with linear fit

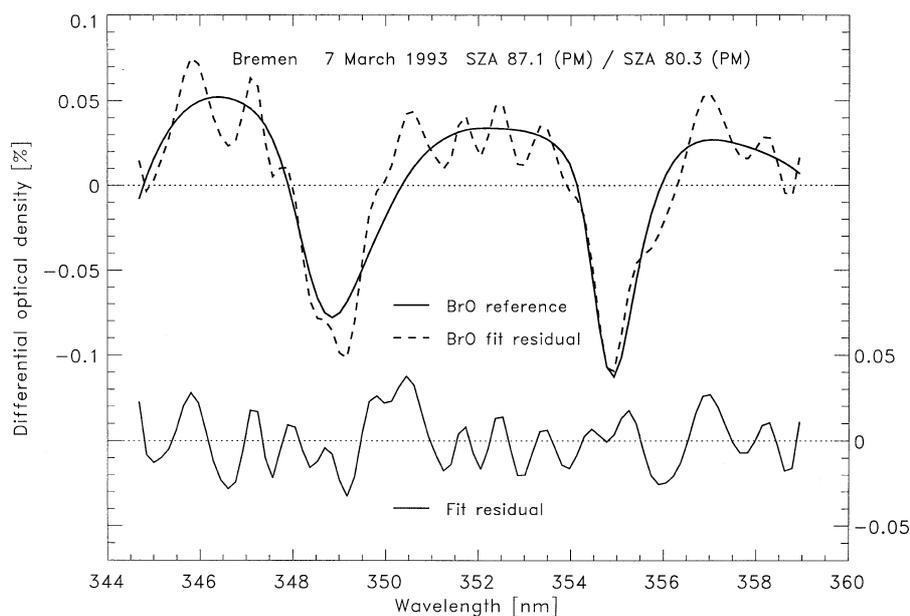


Figure 1. Differential BrO laboratory cross-section and fit residuals. The curve at the bottom is the difference between the two upper ones. This fit yielded a BrO DSCD of $2.0 \cdot 10^{14}$ molecules/cm² having a linear fit error of 5.0 %.

errors below 25 % are presented. Furthermore, days with high NO₂ DSCDs, caused by tropospheric pollution combined with enhanced multiple scattering in clouds, were excluded from the analysis. Finally, as BrO mixing ratios are expected to vary significantly as a function of SZA, it is not considered to be valid to estimate vertical column amounts from the DSCDs without assuming a time-dependent vertical profile for BrO.

2.3. RESULTS

The differential BrO reference spectrum is shown together with the BrO residual for a single fit from 7 March 1993 in Figure 1. The BrO residual was obtained by removing the contributions of O₃, NO₂, Ring effect and scattering from the atmospheric optical density. The fit residual after removing all fitted absorbers (including BrO) is also shown. The residual amounts to no more than 5×10^{-4} from peak to peak. The BrO signal lies clearly above this residual.

For two selected days DSCDs are displayed as a function of solar zenith angle in Figure 2. As noon spectra have been taken as the background, morning and evening values can be compared. On 13 November 1993 DSCDs were nearly symmetrical about noon, the differences between AM and PM values being within the combined error limits. In contrast, on 25 December 1993 DSCDs at dawn exceeded those

at dusk for large SZAs. Taking the observing period as a whole, a systematic difference between morning and evening values can not be inferred.

For the two winters 92/93 and 93/94 BrO DSCDs over Bremen were found to be in the range of 9×10^{13} to 4.5×10^{14} molecules/cm² and to exhibit large day-to-day fluctuations (Figure 3). Arpag *et al.* (1994) measured BrO sunrise DSCDs over Colorado (40°N) which are less than half of the sunrise DSCDs measured simultaneously over Bremen. In contrast, Fish *et al.* (1995) observed BrO sunrise DSCDs above Cambridge (52°N), England, in March 1994 which compare well with the simultaneous measurements above Bremen. However, the maximum values obtained from the Bremen study in December 1993 exceed those previously measured above midlatitudes. This episode of high BrO DSCDs correlates with extremely low stratospheric temperatures over Bremen, as is shown also in Figure 3. A large variability of BrO slant columns is common to all previous measurements.

The disagreement with Arpag *et al.* (1994) is considered unlikely to arise from instrumental inadequacies in either experimental setup. Similarly, the fitting approach is not likely to be a source of error. However, the two experiments use different viewing geometries. During the period of simultaneous AM measurements (22 January to 13 April 1993) the Colorado instrument observed at a line-of-sight zenith angle of 80° towards the west. In consequence, at dawn the observed airmass is on average at larger zenith angles than that observed by the (zenith viewing) Bremen group. Assuming a strong diurnal variation in BrO this would explain the lower DSCDs in Colorado when compared to Bremen. On the other hand the higher effective airmass factor for the Colorado setup should yield higher DSCD values for the same amount of BrO. At present it is unclear whether there was less BrO above Colorado than Bremen or whether the difference between the two measurements results from a strong diurnal BrO variation.

On several days BrO columns were below the detection limit which is estimated from the fit residual to be 1.5×10^{14} molec/cm² in the morning and 1.0×10^{14} molec/cm² in the evening. The difference is explained by lower signals in the AM measurements due to the measurement strategy which is necessary to adapt the integration times to the actual signal levels.

Unfortunately, during February 1994 the spectral resolution of our system was degraded by a thin ice film growing on the cooled detector surface. The latter might have led to a higher detection limit. After this film had been removed on 3 March and stratospheric temperatures had dropped, BrO was clearly detected again. In February 1994 BrO could only be detected for SZAs below 90° so that no DSCDs can be given. At this time 30hPa temperatures over Bremen reached the maximum values in the reporting period. They were unusually high due to a minor warming event over Europe (Naujokat *et al.*, 1994). BrO columns might well be expected to be low at these temperatures.

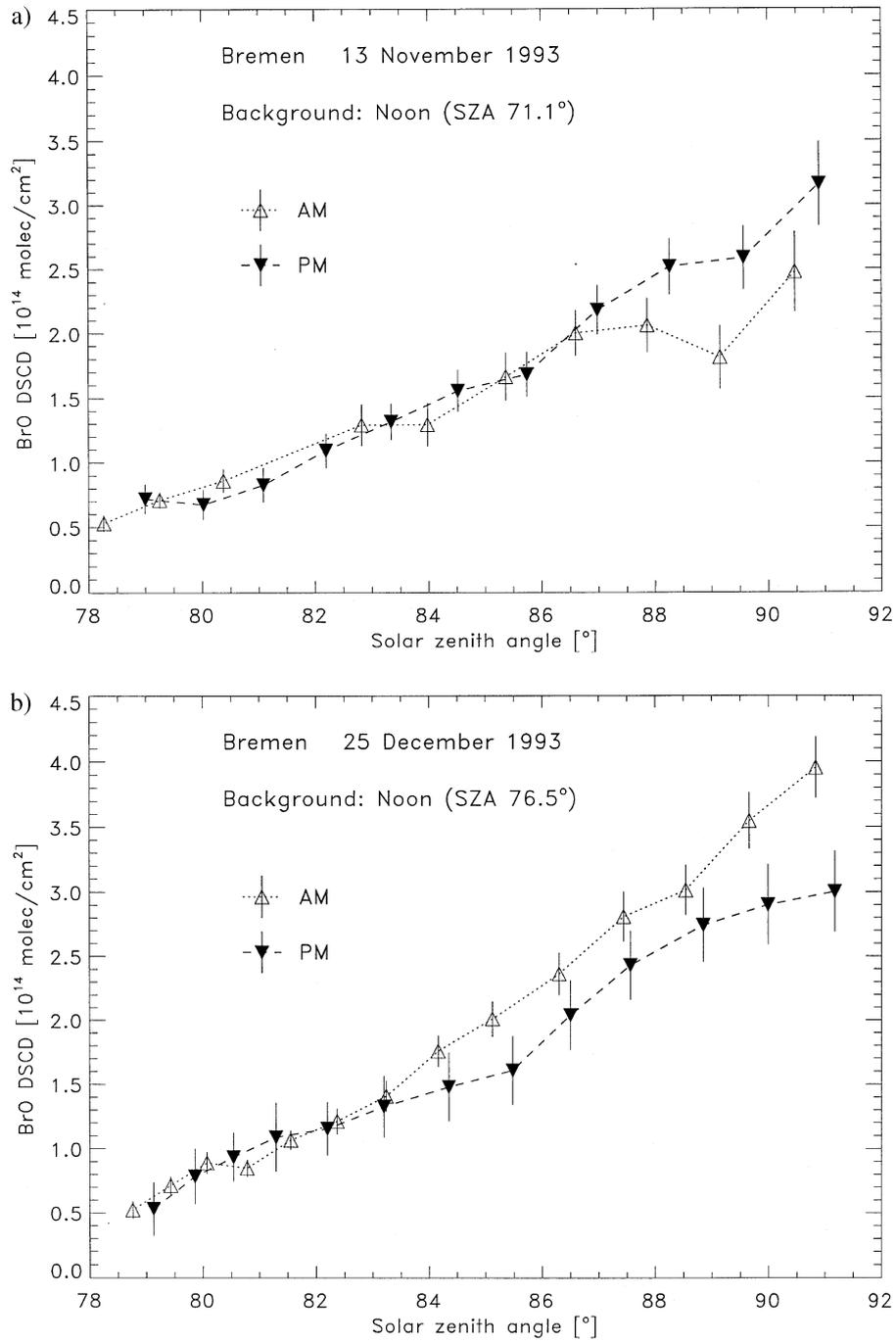


Figure 2. DSCD daytime profiles for BrO. The errorbars indicate the linear fit error only.

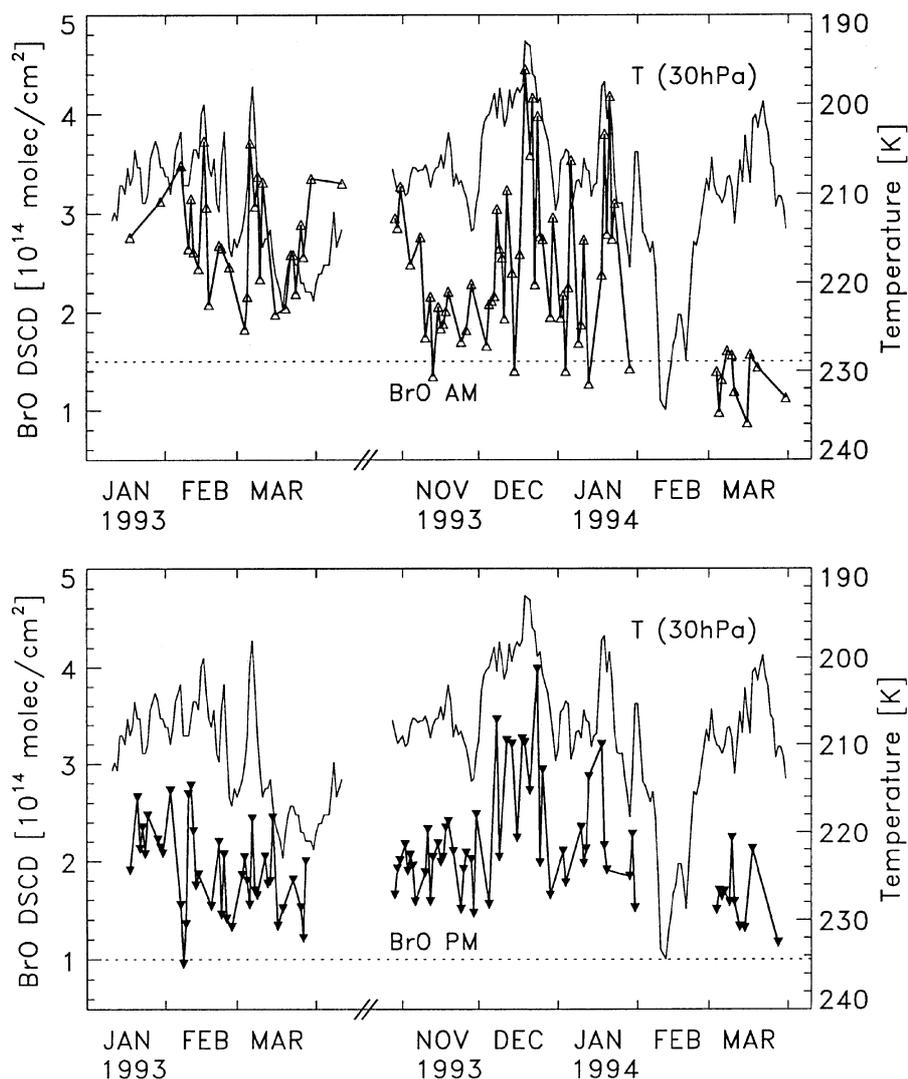


Figure 3. BrO DSCDs for SZA 90°/80° (lines with triangles) together with temperatures at 30 hPa from ECMWF and Berlin analyses. Top: morning, bottom: evening measurements. The dotted lines indicate estimated detection limits for BrO. Note that the temperature axis is inverted.

3. Discussion

Dynamics, gas phase photochemistry, and heterogeneous chemistry together determine BrO mixing ratios at a given location and time. The dataset presented in this work gives some clues to the study of diurnal, daily, and seasonal variations. Year-to-year comparisons are interesting because of the higher stratospheric aerosol loading in the winter of 92/93. Aerosol columns were about three times larger in

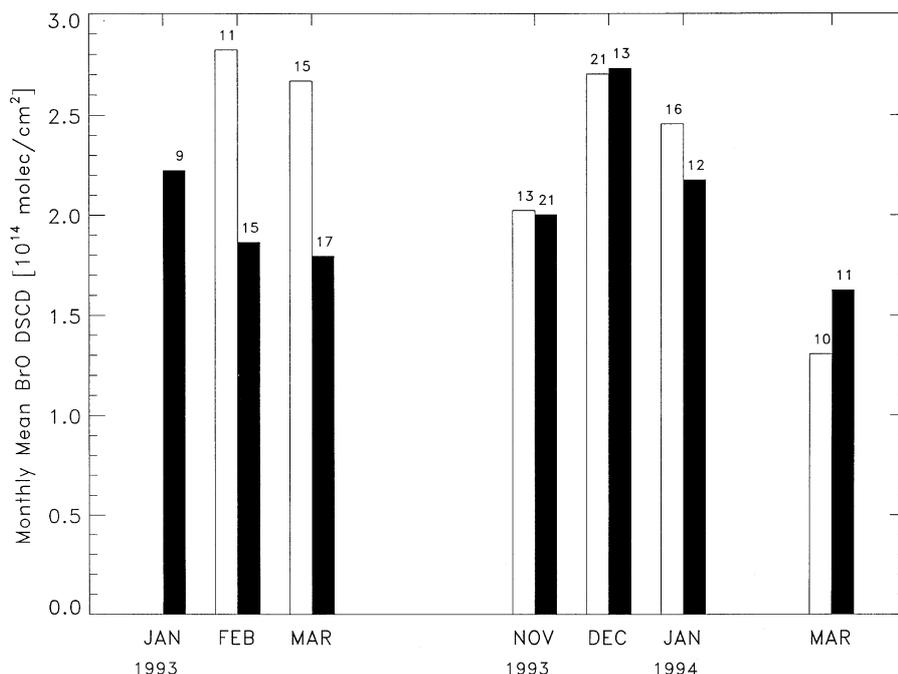


Figure 4. Monthly mean BrO DSCDs. AM: empty bars, PM: filled bars. The numbers indicate the number of days included in the mean. In February 1994 BrO was below the detection limit (see text for details).

the winter of 92/93 compared to 93/94, as shown, e.g., by lidar and sun photometer measurements (Beyerle *et al.*, 1995). This is consistent with a stratospheric lifetime ($1/e$ folding time) of 0.9 years for the Pinatubo aerosol. However, caution is necessary when comparing the BrO data obtained in both winters because of the limited amount of data from the first winter and some modifications to the experiment in summer 1993.

3.1. SEASONAL VARIATIONS

Although the dataset is confined to the November to April period it shows a winter maximum in BrO with a decrease towards spring (Figures 3 and 4). This behaviour is more pronounced in winter 93/94 while in the first months of 1993 the decrease is small. In contrast, Arpag *et al.* (1994) found no trend at all from January to May, 1993. Clearly, a climatology of BrO will only be established from measurements made over several years, including the summer months. These will be treated in a subsequent publication (Richter *et al.*, 1997).

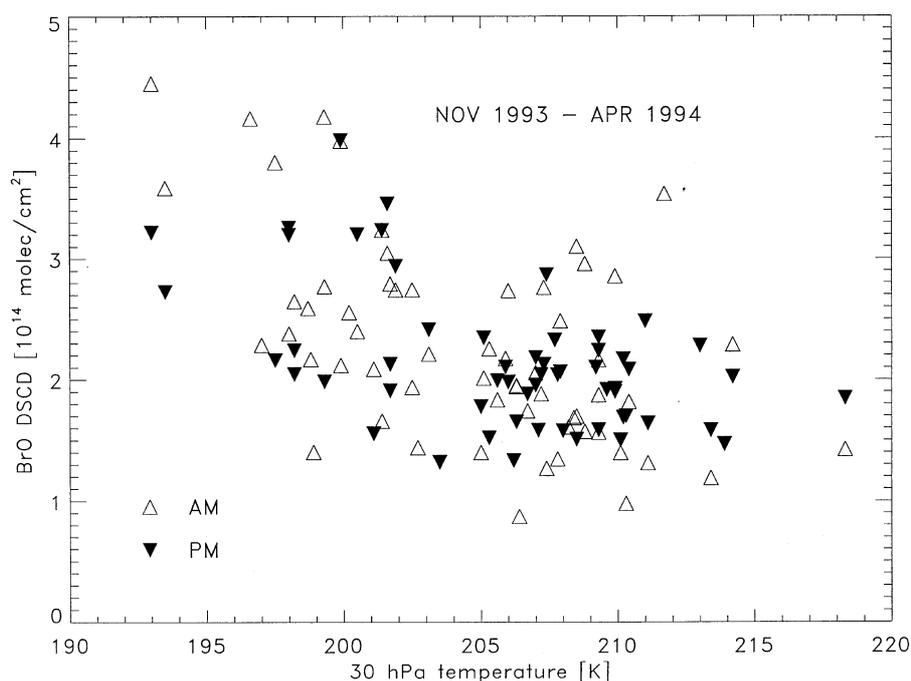


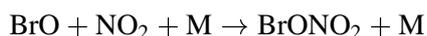
Figure 5. Scatter plot of BrO DSCDs over Bremen in winter 1993/94 and temperatures at 30 hPa.

3.2. DAY-TO-DAY VARIATIONS, TEMPERATURE EFFECTS

The large day-to-day variability seems to be a combined effect of dynamics (advection) and temperature. In addition, vertical displacements of the BrO ‘layer’ induce significant changes in the effective airmass factor (difference of the airmass factors at SZA 80° and 90°) and therefore the corresponding DSCD. Assuming, for illustration, a step profile with no BrO up to a height z_0 and constant BrO mixing ratios above, the effective airmass factor is increased by a factor of two when z_0 is raised from 12 to 16 km. As real BrO vertical profiles are known only insufficiently, no attempt is made to examine the influence of dynamics further in this study.

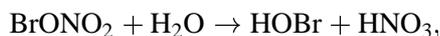
Comparison of the temperatures over Bremen at the 30hPa-level and BrO DSCDs as a function of time (Figure 3) reveals that BrO DSCDs reach their maximum when temperatures fall below 205 K. The anticorrelation at low temperatures is illustrated separately for the second winter by Figure 5. The possible causes of this effect need further consideration.

For homogeneous chemistry, as noted previously by Fish *et al.* (1995), lower temperatures somewhat favour BrONO₂ formation from the gas-phase reaction

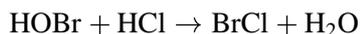


Extrapolating the values recommended in the DeMore *et al.* (1994) compilation to stratospheric temperatures, the rate constant for BrONO₂ formation is increased by a factor 1.47 at 195 K compared to 220 K. This would reduce the BrO stationary state mixing ratios at lower temperatures.

Heterogeneous reactions known to involve bromine are BrONO₂ hydrolysis



which is fast at all temperatures, and



(Hanson and Ravishankara, 1995; Lary *et al.*, 1996). The latter is expected to be more efficient at low temperatures, e.g. below 205 K. (According to Hanson and Ravishankara (1995), laboratory studies quantifying the temperature effect are under way.) The most likely explanation of the observed anticorrelation between BrO DSCDs and temperature at the lower end of observed temperatures arises from the increased production of BrCl during the night and its rapid photolysis at dawn. Note that typical photolytic lifetimes ($1/e$ folding times) of HOBr (53 minutes at an altitude of 17 km, SZA 88°, albedo 0.25) and BrONO₂ (39 minutes) are comparable, but those of BrCl (2.6 minutes) are smaller by more than an order of magnitude. These figures have been calculated using the model PHOTOGT (Blindauer *et al.*, 1996) and absorption cross-sections measured by Deters *et al.* (1996a, 1996b) and Marić *et al.* (1994). The fact that the PM anticorrelation is smaller is in general agreement with this mechanism. By analogy with ClO chemistry the temperature effect might indicate the dominance of heterogeneous chemistry over homogeneous chemistry at least during the night.

3.3. DIURNAL VARIATIONS

Diurnal variations of BrO are expected to be dominated by photochemistry. The behaviour of BrO should be similar to that of other free radicals such as ClO: formation from the nighttime reservoirs during morning twilight, highest mixing ratios during the day, and a decrease in the evening twilight when BrO reacts back into the reservoirs.

The DSCD observed by zenith sky measurements is the product of vertical column density, which decreases with increasing SZA, and the air-mass factor (AMF), which increases with increasing SZA, typically by a factor of 1.5 to 3.5 (depending on the actual BrO height profile) between 80° and 90° SZA. To study diurnal variations, average DSCDs as a function of SZA have been calculated for both winters (Figure 6). PM profiles from both winters are very similar. There is also no significant difference between AM and PM average DSCDs in winter 93/94. In all these cases DSCDs increase with increasing SZA, which means that the AMF increase overcompensates a possible decrease arising from lower photolytic production.

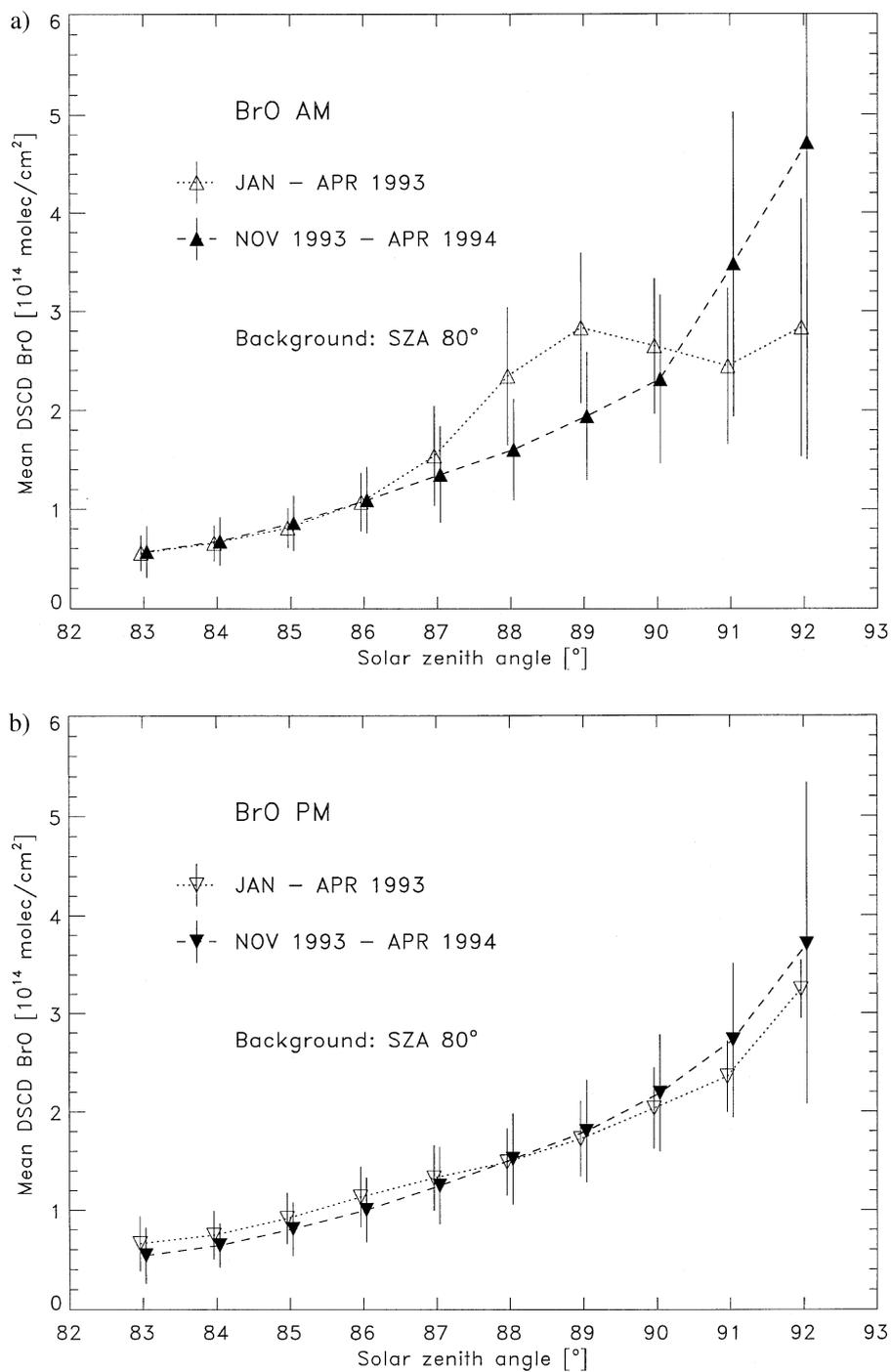


Figure 6. Average DSCD as a function of SZA for BrO, both winters. Top: morning, bottom: evening measurements. The bars represent the 1σ standard deviation of the average. DSCDs have been averaged at integer SZAs. A small SZA offset has been added for clarity only.

The situation is different for the AM values of the first winter. Starting at SZA 92° the DSCD increase slightly to reach a maximum at SZA 89° where it is higher than the corresponding PM value. Thereafter the DSCD drops rapidly reaching values similar to those of the PM data at smaller SZAs. In terms of BrO mixing ratios this can be interpreted as follows. At the end of the night mixing ratios are low. They then build up rapidly until SZA 89° . In the evening the loss of BrO by formation of the nighttime reservoirs starts at lower SZAs but its rate is slower than the photolytically induced production of BrO just after dawn.

Any interpretation has to consider the Pinatubo aerosol loading which was higher in winter 92/93 than in 93/94. As only the AM values behave differently in the two winters, air mass factor changes induced by the higher aerosol loading are not a sufficient explanation. BrCl as possible nighttime reservoir is only important for temperatures below 210 K (which, however, occur in both winters). The precise mechanism by which the elevated early morning production of BrO, first observed in this study occurring during the 1993 winter months, cannot be unambiguously established. However such an effect requires the rapid photolysis of a photo-labile Br-reservoir gas even at relatively low SZAs. The most likely candidates are therefore the gases BrCl or Br₂ which can be formed by heterogeneous reactions. On balance it seems most probable that the anomalous AM behaviour of BrO and associated nighttime production of a photo-labile species arises from enhanced aerosol loading during the winter of 1992/93 compared with winter 1993/94.

4. Summary

DSCDs for the BrO radical have been measured from the ground at a mid-latitude site in winter and early spring of the years 1993 and 1994. The large variability of the DSCDs seen in this study is similar to that found in earlier works. The absolute values are in good agreement with simultaneous measurements of Fish *et al.* (1995) above England while Arpag *et al.* (1994) measured DSCDs above Colorado which were lower by a factor of more than 2.

Morning and evening behaviours were in most cases similar. At low temperatures, BrO DSCDs were found to be anticorrelated with temperatures at 30 hPa which is best attributed to the temperature dependence of the HOBr + HCl reaction on or in sulfate aerosols. The influence of dynamics on the variability of the measured BrO DSCDs has to be investigated.

Finally it is clear that the present set of BrO measurements is an incomplete basis for the provision of a full understanding of Br cycling in the stratosphere. A complete understanding of the chemical behaviour of bromine compounds requires both *in situ* snapshots of particular air masses and long-term remote sensing data from the ground and global data from satellite platforms.

Acknowledgements

Parts of this work have been funded by the University of Bremen, the European Union (SCUVS projects) and the German Space Agency (DARA). We are grateful to U. Platt, D. Perner, and H. Frank for assistance establishing this project and for useful discussions. We thank B. Naujokat (FU Berlin) and P. von der Gathen (AWI Potsdam) for kindly providing meteorological data. This work also benefitted from the talks and discussions during the 3rd European Symposium on Polar Stratospheric Ozone in Schliersee.

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