Midlatitude observations of the diurnal variation of stratospheric BrO

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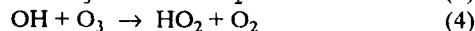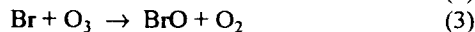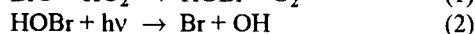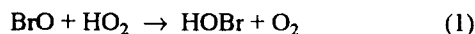
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Abstract. The diurnal variation of BrO through sunrise and sunset has been measured above Cambridge, England, (52°N) during March and April 1994 using zenith sky spectroscopy. The measured BrO slant column at 90° solar zenith angle (SZA), relative to that at 80° SZA, is typically 1.5×10^{14} cm^{-2} but varies significantly from day to day. The average variation of BrO slant column with SZA through sunrise and sunset is in good agreement with predictions from a photochemical model, coupled to a radiative transfer model. The zenith sky measurements are consistent with in situ measurements of BrO concentrations and indicate that the inorganic bromine content of the stratosphere is 18-24 parts per trillion by volume (pptv).
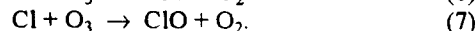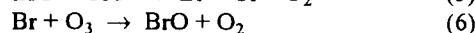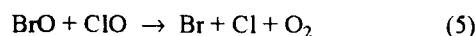
1. Introduction

Since 1979, ozone abundances at midlatitudes have been decreasing by around 0.5% per annum [*Stolarski et al.*, 1992], with maximum ozone depletion occurring in the low stratosphere [*WMO*, 1994]. A number of mechanisms to explain the observed ozone losses have been proposed, including the export of air from the polar vortex [*Tuck*, 1989], ozone destruction in the subvortex region [R.L. Jones and I. Kilbane-Dawe, The influence of the stratospheric subvortex region on midlatitude composition, submitted to *Geophysical Research Letters*, 1995] and in situ ozone loss. However, as discussed in *WMO* [1994], it is difficult to quantify the magnitude of the ozone destruction due to these different processes.

The abundances of the radicals responsible for in situ ozone depletion have recently been measured as part of the Stratospheric Photochemistry, Aerosols and Dynamics Experiment (SPADE) [*Wofsy et al.*, 1994]. These measurements have shown that catalytic cycles involving HO$_x$ (which has natural sources) are responsible for the majority of ozone destruction in the low stratosphere at midlatitudes [*Wennberg et al.*, 1994]. The SPADE measurements also showed that halogen radical chemistry accounts for a third of ozone destruction in this region and that bromine is involved in half of this destruction via catalytic cycles involving HO$_x$

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{1}$$
$$HOBr + h\nu \rightarrow Br + OH \tag{2}$$
$$Br + O_3 \rightarrow BrO + O_2 \tag{3}$$
$$OH + O_3 \rightarrow HO_2 + O_2 \tag{4}$$

and ClO

$$BrO + ClO \rightarrow Br + Cl + O_2 \tag{5}$$
$$Br + O_3 \rightarrow BrO + O_2 \tag{6}$$
$$Cl + O_3 \rightarrow ClO + O_2. \tag{7}$$

The reaction of BrO with ClO has three pathways, two of which (those forming Br+Cl+O$_2$ and BrCl + O$_2$) result in ozone destruction, while a third (forming OClO) is a null cycle resulting in no loss of odd oxygen. The possibility of ozone destruction via catalytic cycles involving iodine has also been suggested [*Solomon et al.*, 1994]. Man's activities have caused the stratospheric abundances of chlorine and, to a lesser extent, bromine to increase during the past few decades, thus halogen-catalysed ozone destruction is likely to have increased at midlatitudes.

In situ BrO concentrations have been measured using a resonance fluorescence instrument [*Brune et al.*, 1988]. However, stratospheric BrO concentrations are small and long integration periods (exceeding 20 min) are necessary. The in situ measurements are thus unsuited to investigating the variation of BrO concentrations through twilight, an interesting period since the rate at which BrO is converted to and released from its nighttime reservoirs provides information on the nature of those reservoirs. BrO can also be measured using ground-based UV visible spectroscopy [*e.g.*, *Solomon et al.*, 1989; *Wahner and Schiller*, 1992], and there is one previous measurement of BrO columns at midlatitudes [*Arpag et al.*, 1994].

In this paper, slant columns of BrO above Cambridge (52° N), measured using UV visible spectroscopy, are presented. The observed diurnal variation of BrO slant columns through twilight is compared with predictions from a photochemical model, coupled to a radiative transfer model, and the implications of the study for the amount of bromine in the stratosphere and the nighttime bromine reservoirs are discussed.

2. Measurements of the Diurnal Variation of BrO

2.1. Method

BrO is measured using a spectrometer which views light from the zenith sky (in the one previous measurement of BrO at midlatitudes, *Arpag et al.* [1994] viewed light from 10° above the horizon in the direction of the sun). Light entering the instrument is focused onto the entrance slit of an f/4 Czerny Turner spectrometer. Spectra are recorded between

320 and 390 nm at a resolution (FWHM) of 0.7 nm. A charge coupled device (CCD) that is cooled to ensure negligible dark current is used as the detector. Unlike diode array detectors, which are conventionally used for UV visible spectroscopy, the CCD detector used does not suffer from etaloning [Mount et al., 1992] and has a very small readout noise. However, it does have a significant pixel-to-pixel variability (~2%).

The spectral analysis procedure [Fish, 1994] involves fitting differential cross sections due to O_3, NO_2, O_4, BrO, Rayleigh scattering and the Ring effect to the measured difference in optical depth between two zenith sky spectra. The absorption cross sections of O_3 and NO_2 were measured in the laboratory at -65°C using the spectrometer from the zenith sky instrument. These absorption cross sections are multiplied by a wavelength-dependent air mass factor, which accounts for light at different wavelengths being scattered from different altitudes, prior to being fitted to the measured optical depth [Fish, 1994]. The absorption cross sections of BrO and O_4 were taken from Wahner et al. [1988] and Greenblatt et al. [1990] and convolved to the instrument resolution. The ring cross section was simulated using a model of Raman scattering in the atmosphere [Fish and Jones, 1995].

Twilight zenith sky spectra were analysed using a reference spectrum measured at 80° solar zenith angle (SZA) during the same morning or evening. The analysis was performed between 345 and 365 nm. Although the main BrO absorptions occur at 349 and 355 nm, NO_2 absorptions occur throughout the 345- to 365- nm interval and the region from 357 to 365 nm was included to minimize the possibility of correlations between the BrO and NO_2 absorptions. In Figure 1 is shown the observed and fitted optical depths of BrO. The amount of BrO retrieved at 90° SZA was found to be uncorrelated with the retrieved amounts of any other absorber.

2.2. Results

In Figure 2 the variation of BrO slant column with SZA through sunrise (relative to the BrO slant column at 80° SZA) is shown on days 70, 76, and 80 of 1994. These days were chosen to illustrate the range of BrO slant column amounts
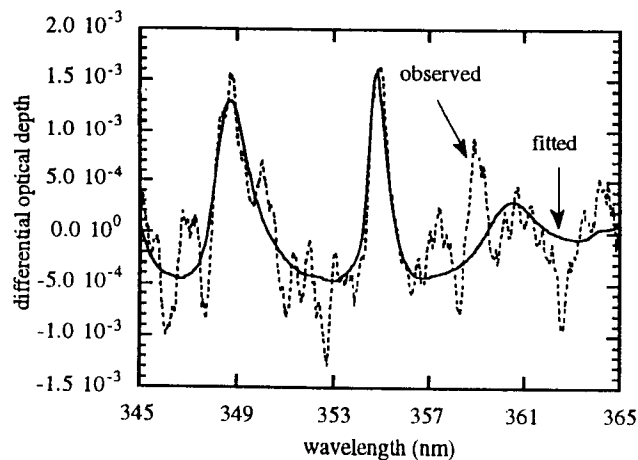

Figure 2. The diurnal variation of BrO slant columns through sunrise (relative to 80° SZA) for days 70, 76, and 80 of 1994.

Figure 1. The fitted optical depth of BrO, and the measured optical depth after the absorptions due to O_3, NO_2, O_4, Ring and Rayleigh were subtracted, leaving only the absorption due to BrO.
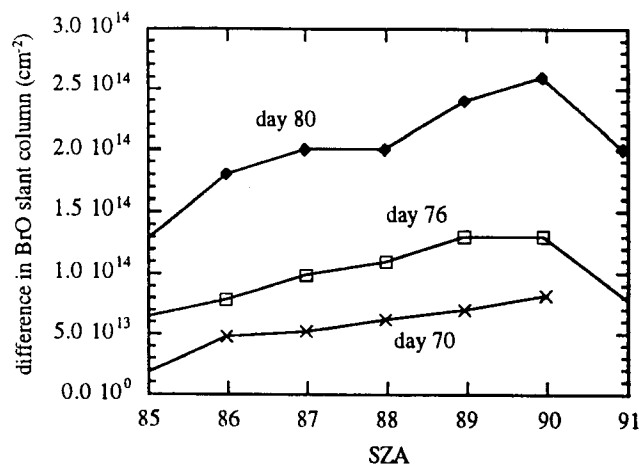
observed. The smooth variation of BrO slant column with SZA indicates that the random error on the measured slant columns is small. At sunrise, the BrO slant column peaks at 90° SZA, while at sunset, the BrO slant column increases monotonically with SZA. The measurements also show considerable day-to-day variability, as illustrated in Figure 3, which shows a time series of the difference in BrO slant column between 90° and 80° SZA in the morning. A sunset time series is similar, but shows slightly greater day-to-day variability. The magnitude of the error bars (±15%) is somewhat arbitrary, since the residuals are dominated by systematic structure whose effect on the retrieved BrO abundances is practically impossible to quantify. The day-to-day variability of measured BrO slant columns is believed to be genuine.

The BrO slant columns measured above Cambridge (52°N) are slightly larger than those previously measured above Colorado (40°N), but this is consistent with model predictions (see section 5) that twilight BrO column abundances should increase with latitude. BrO slant columns measured at the two mid-latitude sites show a similar day-to-day variability. In order to compare the measured diurnal variation of BrO with model predictions, the average variation of BrO slant column with SZA was calculated at sunrise and sunset.

3. Bromine Chemistry

In the absence of polar stratospheric cloud (PSC) processing, most inorganic chlorine is held in the reservoirs HCl and $ClONO_2$. By contrast, HBr is not a major bromine reservoir [Traub et al., 1992] since bromine atoms do not react with CH_4 or H_2. In addition, the production of HBr from the reaction of HO_2 with BrO has been recently found to be negligible throughout the stratosphere [Mellouki et al., 1994]. In the stratosphere, $BrONO_2$ is photolyzed more readily than $ClONO_2$, since its absorption cross section is similar to that of $ClONO_2$ but is shifted to longer wavelengths [Spencer and Rowland, 1978; Rowland et al., 1976]. The products of $BrONO_2$ photolysis are unknown but by analogy with chlorine are likely to be

$$BrONO_2 + h\nu \rightarrow BrO + NO_2 \tag{8}$$
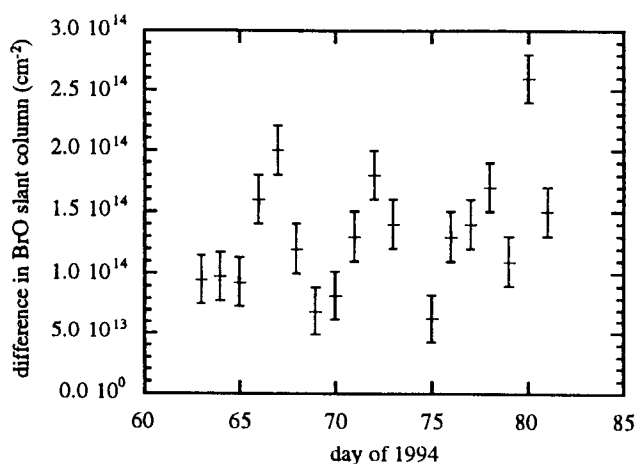$$BrONO_2 + h\nu \rightarrow Br + NO_3. \tag{9}$$
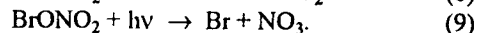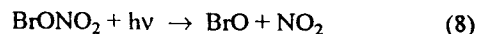
Figure 3. A time series of the difference in BrO slant column between 80° and 90° SZA measured at sunrise.

Since NO_3 is readily photolyzed and Br atoms react rapidly with O_3 to form BrO at altitudes below 40 km, (8) and (9) have the same end result. BrO and $BrONO_2$ are thus the major bromine species in the stratosphere during the day. HOBr is only a significant bromine reservoir in the upper stratosphere.

At sunset, BrO is converted to $BrONO_2$ by the termolecular reaction

$$BrO + NO_2 + M \rightarrow BrONO_2 + M. \qquad (10)$$

Although (10) is the dominant loss process for BrO at twilight, a small amount of BrO reacts with ClO (from $ClONO_2$ photolysis) to form BrCl

$$BrO + ClO \rightarrow BrCl + O_2. \qquad (11)$$

Provided the two nighttime bromine reservoirs do not react further during the night, BrO will be released at sunrise as $BrONO_2$ and, to a lesser extent, BrCl are photolyzed.

A number of recent laboratory studies have shown that certain bromine reservoirs can take part in heterogeneous reactions on both PSCs [*Abbatt*, 1994] and on sulphate aerosol [*Hanson and Ravishankara*, 1995]. The most important of these reactions is the hydrolysis of $BrONO_2$ in sulphate aerosol

$$BrONO_2 + H_2O \rightarrow HOBr + HNO_3, \qquad (12)$$

a reaction which proceeds readily (γ=0.4) regardless of temperature [*Hanson and Ravishankara*, 1995]. $BrONO_2$ hydrolysis will thus be significant throughout the year, at all latitudes. For a typical background aerosol surface area (1 μ m^2 cm^{-3}), $BrONO_2$ would be converted to HOBr on a timescale of 12 hours.

The HOBr produced by $BrONO_2$ hydrolysis can then react with HCl dissolved in the sulphate aerosol [*Hanson and Ravishankara*, 1995]

$$HOBr + HCl \rightarrow BrCl + H_2O. \qquad (13)$$
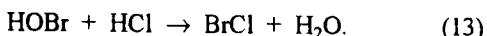
However, the solubility of HCl in sulphuric acid aerosol is a strong function of temperature [*Luo et al.*, 1994] and

increases rapidly at temperatures approaching, from above, the threshold for nitric acid trihydrate (NAT) formation. Consequently, the heterogeneous conversion of HOBr to BrCl is only expected to be important at temperatures below 200 K. At these low temperatures, (13) has the potential to convert bromine into the photolabile compound BrCl and to convert chlorine from the reservoir compound HCl into the active form, ClO.

Photochemical model calculations (described below) predict that the stratospheric vertical columns of BrO and $BrONO_2$ will vary markedly through twilight, as shown in Figure 4. The model run includes the hydrolysis of N_2O_5 on sulphate aerosol but does not include heterogeneous bromine chemistry. At large SZAs, the model predicts that more BrO is present at sunset than sunrise. This asymmetry indicates that BrO and $BrONO_2$ are not in steady state. At sunset, actual BrO concentrations exceed steady state concentrations, and are determined by the rate of reaction of BrO with NO_2. At sunrise, BrO concentrations are limited by the rate at which the nighttime bromine reservoir ($BrONO_2$ in the model) is photolyzed. Measurements at sunrise and sunset
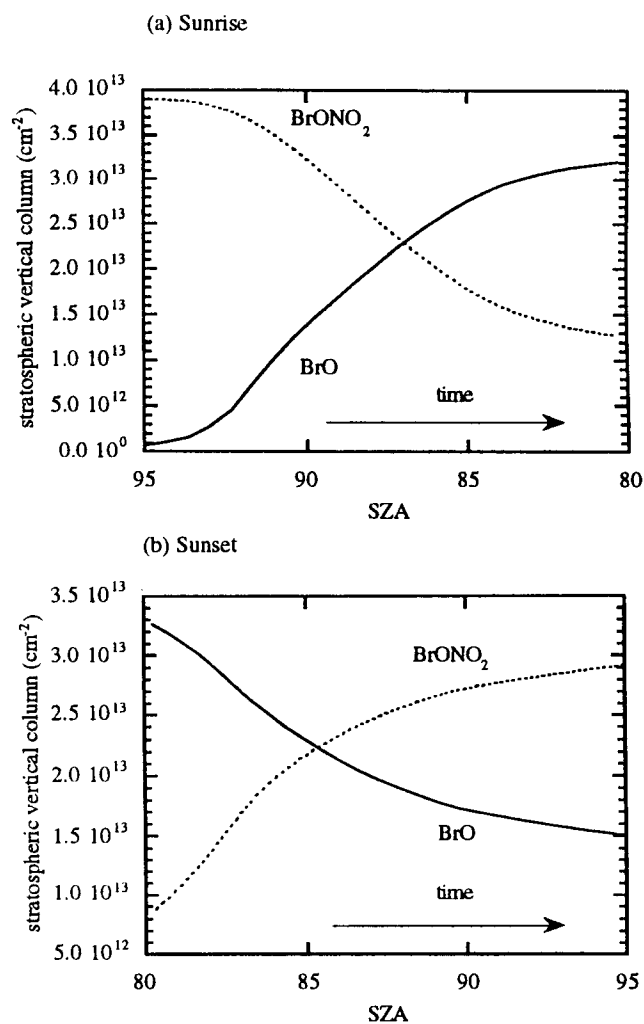
(a) Sunrise

(b) Sunset

Figure 4. The variation of the stratospheric vertical columns of BrO and $BrONO_2$ through sunrise and sunset, at 52°N during January, predicted by a chemical model including gas phase bromine chemistry and the heterogeneous hydrolysis of N_2O_5.

thus provide complementary information on bromine abundances, NO_2 abundances and the nature of the nighttime bromine reservoir.

Arpag et al. [1994] obtained reasonable agreement between BrO slant columns measured over Colorado and BrO slant columns which were calculated using the assumption that BrO does not vary through twilight. Arpag *et al.* calculated the shape of the variation of BrO slant column with SZA for a number of BrO profiles and concluded that their measurements could be explained by a uniform BrO mixing ratio of 5 parts per trillion by volume (pptv) above 12 km. However, since BrO concentrations change rapidly through twilight, even at 80° SZA, a model prediction based on the correct vertical profile of Br_y will not reproduce the observations unless the photochemical change in BrO concentrations is accounted for. Allowing the vertical profile of BrO to vary will merely allow a false profile of BrO, which coincidentally fits the observations, to be retrieved. In section 4, the use of coupled photochemical and radiative transfer models to predict the variation of BrO slant column through twilight will be described.

3.1. Accuracy of Laboratory Data

The rates of some of the photochemical reactions which control BrO abundances are subject to considerable uncertainties. The rate of reaction of BrO with NO_2 is not accurately known, being $(4.2\pm0.8)\times10^{-31}(T/298)^{-2.0\pm0.5}$ [*Danis et al.*, 1990]. The absorption cross section of $BrONO_2$ has recently been remeasured [J.B. Burkholder et al., UV/visible and IR absorption cross sections of $BrONO_2$, submitted to *Journal of Geophysical Research*, 1994] and the long wavelength tail of the absorption found to extend to 500 nm. The absorption cross section of HOBr has been measured recently and is considered accurate to within ~10% [*Orlando and Burkholder*, 1995].

4. Modeling the Diurnal Variation of BrO at Midlatitudes

4.1. Photochemical Model

AutoChem, a chemical box model written by D.J. Lary [*Lary et al.*, 1995], was used to model the diurnal variation of
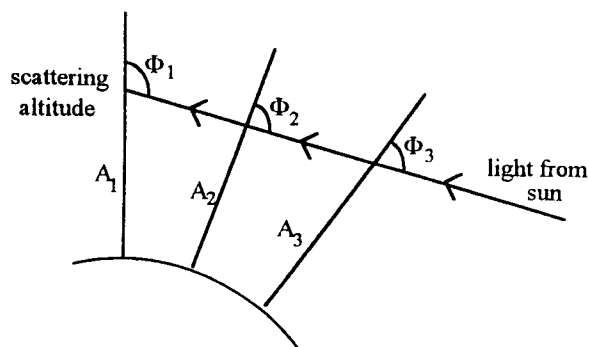
Figure 5. The variation of solar zenith angle with location in the atmosphere for a ray of sunlight entering the atmosphere during twilight. Both Φ (the local SZA) and A (the local altitude) vary along the ray's path between the sun and the scattering point.
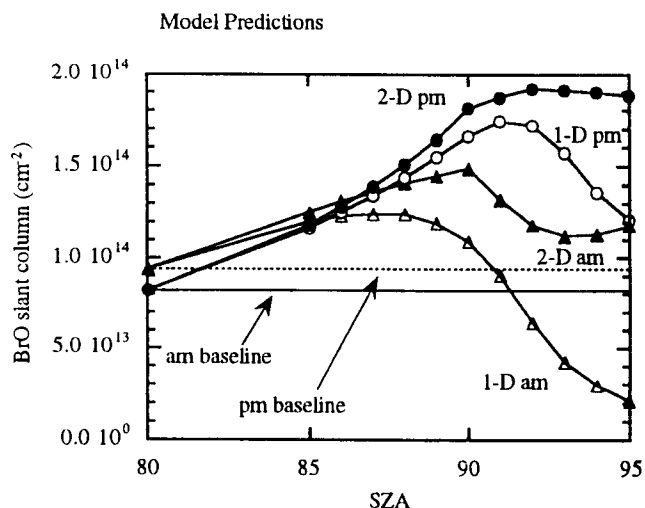
Model Predictions

Figure 6. The effect of a two-dimensional BrO field on the BrO slant column predicted by the model.

BrO. The model is used as a one-dimensional model by considering 14 levels in the vertical, extending from the ground to 50 km. The equations expressing the rate of change of species concentrations are integrated numerically without resort to the family approximation, which is least accurate at twilight.

Bromine is transported into the stratosphere in the form of organic bromine compounds. Measurements of the vertical distributions of CH_3Br, $CBrClF_2$, and $CBrF_3$ in the Arctic show that the mixing ratios of these compounds decrease markedly from their tropospheric values at 10 km to essentially zero above 20 km [*Fabian et al.*, 1994]. At midlatitudes, the vertical profile of methyl bromide (CH_3Br) was observed to fall off between 14 and 24 km. The absolute calibration of Fabian et al.'s measurement of methyl bromide, the main source of stratospheric bromine, is uncertain, so the measurements constrain the vertical profile of inorganic bromine but not the absolute amount. Inorganic bromine mixing ratios of 16 ± 4 pptv between 12 and 20 km were inferred by *Salawitch et al.* [1988] from observations of OClO during the National Ozone Experiment (NOZE) [*Solomon et al.*, 1987a]. Thus the vertical profile of inorganic bromine (Br_y) in the model was initially constrained to increase linearly from 0 pptv at 14 km to 15 pptv at 24 km, and to remain constant at 15 pptv above 24 km. The amount of Br_y in the model was subsequently varied but the shape of the vertical profile remained the same.

The twilight variation of BrO is affected by NO_2 concentrations which, in turn, are dependent on the surface area of sulphate aerosol present. During the winter of 1993-1994, stratospheric aerosol abundances were still decreasing, following the eruption of Mount Pinatubo, 30 months earlier. The aerosol surface area used in the model was taken from measurements by a balloonborne particle counter over Laramie, Wyoming (41°N), during March 1994 [*Hofmann et al.*, 1994]. A peak aerosol surface area of 7.5 $\mu m^2 cm^{-3}$ was observed at that time, located between 12 and 17 km. The vertical profile of aerosol surface area inferred from SAGE measurements during 1989 [*WMO*, 1991] was linearly scaled to match this peak surface area.

The vertical profiles of $ClONO_2$ and HCl in the one-dimensional model were taken from *Webster et al.* [1994].

All other species in the one-dimensional model were initialized with chemical mixing ratio profiles taken from the Cambridge two-dimensional model [*e.g.*, *Pyle and Rodgers*, 1980]. The majority of the kinetic and photochemical data used by the one-dimensional model was taken from *Atkinson et al.* [1992] and *De More et al.* [1992]. Heterogeneous bromine reactions are included in the model [D.J. Lary *et al.*, Atmospheric Heterogeneous Bromine Chemistry, submitted to *Journal of Geophysical Research*, 1995] and their rates were taken from *Hanson and Ravishankara* [1995].

In order to predict the variation of BrO slant column with SZA, the one-dimensional model was initialized and integrated for 8 days at a latitude of 52.5°N with temperatures and solar illumination appropriate for March 5. BrO mixing ratios were output on 13 pressure levels at 3 min intervals for solar zenith angles between 80° and 95° in the morning and evening of the last day of the integration. The BrO mixing ratios were then used by the zenith sky forward model to calculate BrO slant columns as a function of SZA.

4.2. Calculation of BrO Slant Columns

There are then two possible ways to compare the measured and modeled BrO abundances: air mass factors (AMFs) may be calculated and used to convert the measured BrO slant columns to vertical columns; or the model results may be converted to BrO slant columns which are then compared directly with the measured BrO slant columns. In the following discussion, predicted and measured slant columns are always compared for two reasons. First, and most important, the vertical column of BrO is not well defined because BrO abundances vary with SZA, and the SZA varies along the path of the light through the atmosphere. This is illustrated in Figure 5. Second, if any changes are made to the model, the AMFs used to convert measured BrO slant columns to vertical columns will change. This makes it more difficult to compare different model scenarios, since any change to the model will cause both the predicted and the measured BrO vertical columns to change.

The first step in predicting the BrO slant column at a particular SZA is to calculate the amount of sunlight which is scattered in to the instrument from each altitude, and the
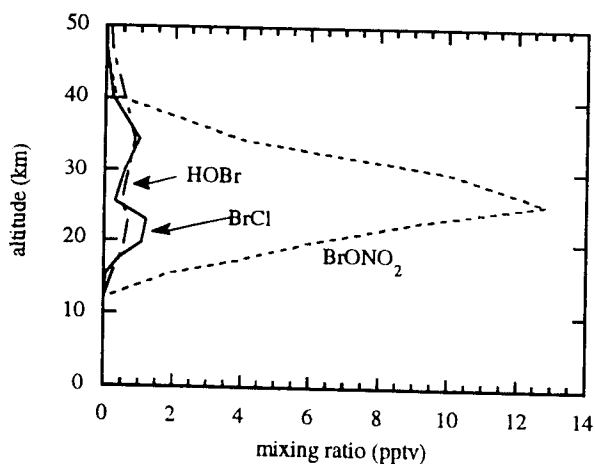

(a) gas-phase bromine chemistry
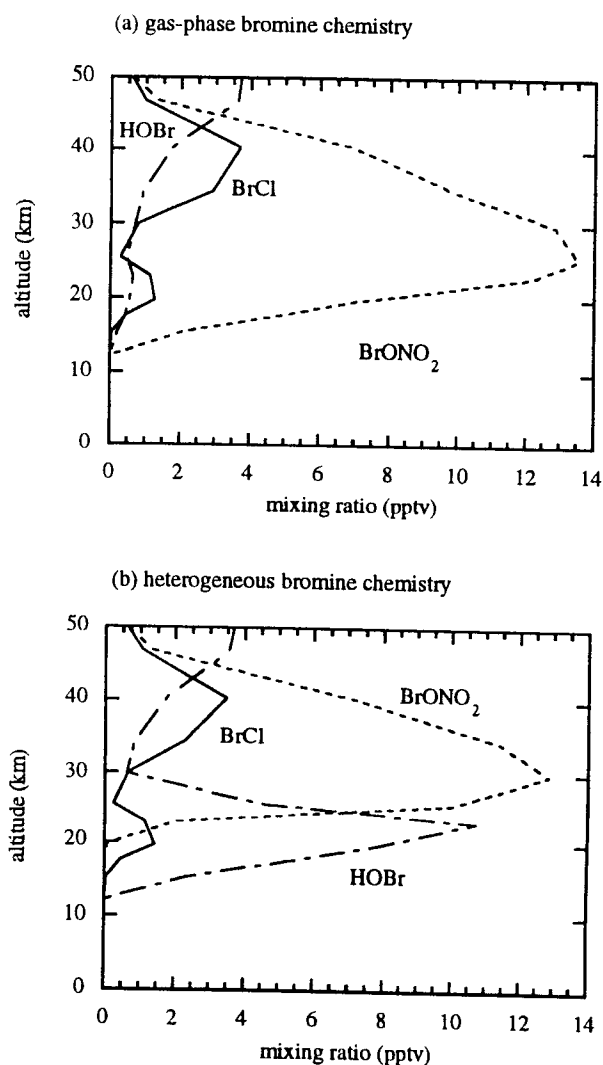
(b) heterogeneous bromine chemistry

Figure 8. The vertical profiles of $BrONO_2$, HOBr, and BrCl, prior to sunrise, as predicted by the one-dimensional model. Plot (a) shows the effect of gas phase chemistry; plot (b) shows the effect of heterogeneous bromine chemistry.

geometry of the light path traversed by rays of light between the sun and each scattering point (refer to Figure 5). A single scattering model, similar to that described by *Solomon et al.* [1987b], is used. The atmosphere is divided into 80 layers, each 1 km thick. The amount of BrO in each layer is taken from the output of the photochemical model. At any given scattering altitude, the slant column of BrO is calculated as the sum of contributions from each layer the light traverses. BrO slant columns for different scattering altitudes are then combined to give the overall BrO slant column.

Although the BrO concentration is allowed to vary with altitude, that is, from one layer of atmosphere to the next, the layers are usually assumed to be horizontally homogeneous and the BrO concentration corresponding to the SZA vertically above the instrument is used (the one-dimensional slant column calculation). However, since the local SZA changes along the slant path (Figure 5), the BrO concentration appropriate for that altitude and local SZA should be taken at any point on the path, as discussed by *Solomon et al.* [1989] and *Wahner and Schiller* [1992].

Figure 7. The vertical profiles of $BrONO_2$, HOBr, and BrCl predicted by the model just after sunset. Above 30 km, BrO is still the major bromine species.

The inclusion of this two-dimensional BrO field has a large effect on the predicted variation of BrO slant column with SZA, as shown in Figure 6. The effect of including the two-dimensional BrO field is most marked when the difference in BrO slant column between 80° and 90° SZA is considered: this is the quantity that is retrieved from zenith sky spectra. At sunrise, the inclusion of the two-dimensional BrO field causes the difference in BrO slant column between 80° and 90° SZA to be twice as large as when the one-dimensional BrO field is used. As shown later, the two-dimensional calculation brings both the shape and the magnitude of the predicted BrO slant columns into much better agreement with observations.

4.3. Model Calculations of the Nighttime Partitioning of Br$_y$

During sunset, BrO is converted to BrONO$_2$ and BrCl. The vertical profiles of these species soon after sunset (95° SZA), as predicted by the one-dimensional model, are shown in Figure 7. The vertical profile of Br$_y$ used in these calculations increases from 0 pptv at 14 km to 15 pptv at 24 km and above. The model predicts that BrONO$_2$ is the major bromine reservoir after sunset, with a peak abundance of 13 pptv, and that there is a small but significant amount of BrCl, 1.5 pptv. A model run which includes only gas phase bromine chemistry predicts that during the night, more BrONO$_2$ is formed at higher altitudes, but the partitioning of Br$_y$ immediately prior to sunrise is similar to that at the beginning of the night, as shown in Figure 8(a). When heterogeneous bromine reactions are included (i.e. BrONO$_2$ hydrolysis), the one-dimensional model predicts that most of the BrONO$_2$ in the low stratosphere is converted to HOBr during the night. The vertical profiles of BrONO$_2$, HOBr, and BrCl immediately before sunrise, predicted by the model which includes BrONO$_2$ hydrolysis, are shown in Figure 8(b).

5. Comparison Between Model Predictions and Observations

5.1. Average Variation of BrO Slant Column with SZA

Since BrO slant columns measured on different days differ significantly, average BrO slant columns (relative to 80° SZA) were determined and are shown in Figure 9. The error bars represent the standard deviation of the average. At sunset, the average BrO slant column increases monotonically with increasing SZA, reaching a value of 2.3×10^{14} at 91° SZA. By contrast, as the sun rises (and the SZA decreases), the BrO slant column increases to a maximum of 1.4×10^{14} at 90° SZA, then decreases with decreasing SZA. At SZAs smaller than 89°, the average BrO slant columns measured at sunrise and sunset do not differ significantly, in common with previous observations.

The variation in BrO slant column predicted by the model is also shown in Figure 9. At sunset, measured BrO slant columns are in good agreement with model predictions assuming 21 pptv of Br$_y$ in the stratosphere. The excellent agreement with the shape of the predicted diurnal variation of BrO slant columns confirms the ability of the model to simulate the chemistry occurring; only the absolute amount of Br$_y$ in the stratosphere has been changed to fit the observations. Sunset BrO abundances are governed mainly by the rate of BrONO$_2$ formation (10) and the good agreement between model and measurements suggests that the rate
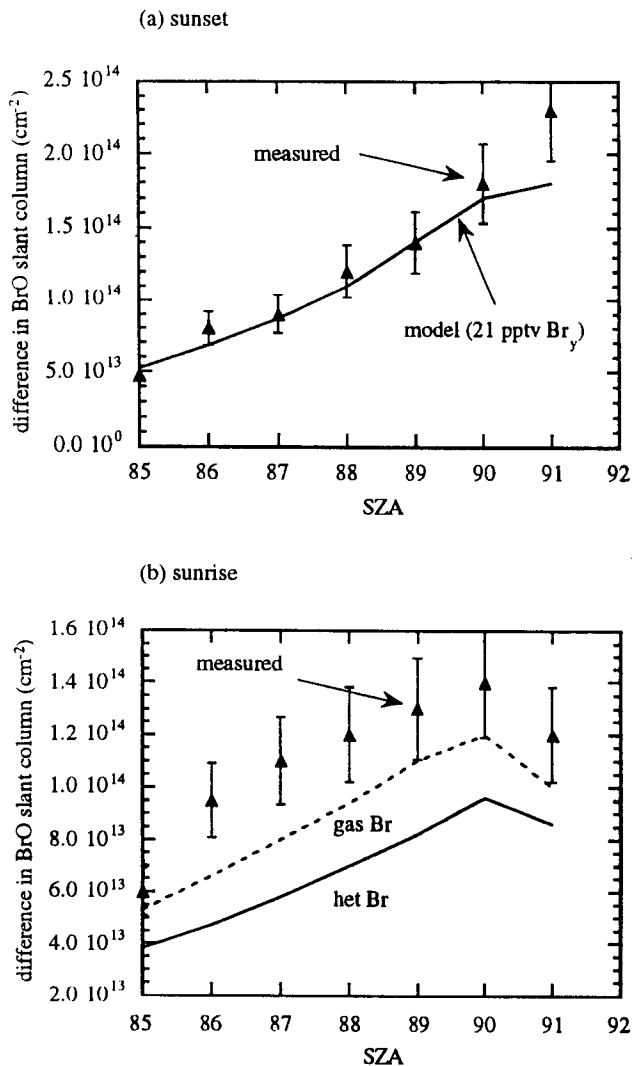

(a) sunset

(b) sunrise

Figure 9. A comparison between measured BrO slant columns and model predictions at sunrise and sunset. The model predictions include the new BrONO$_2$ cross section and the two-dimensional BrO field.

constant for (10) is reasonably accurate and the model is correctly predicting the amount of NO$_2$ in the stratosphere.

Sunrise BrO abundances are governed by the rate of photolysis of the nighttime bromine reservoirs. When only gas phase bromine chemistry is considered, BrONO$_2$ is predicted to be the main nighttime bromine reservoir; when BrONO$_2$ hydrolysis on sulphate aerosol is included, HOBr becomes the main bromine reservoir in the low stratosphere immediately before sunrise. Since the photolysis frequency of HOBr is smaller than that of BrONO$_2$, the model predicts slightly smaller BrO slant columns at sunrise when BrONO$_2$ hydrolysis is included. The two cases are shown in Figure 9.

BrO slant columns predicted at sunrise would be much larger if BrCl, rather than BrONO$_2$ or HOBr, was the main nighttime bromine reservoir, because BrCl is more readily photolyzed. BrCl can be formed from HOBr via (13), but the amount of BrCl formed depends critically on the temperature. However, temperatures over Cambridge during March were never low enough for significant BrCl to be formed by (13).

5.2. Sensitivity to Model Assumptions

At sunset, the predicted variation of BrO slant column is dependent on the vertical profiles of NO_2 and Br_y used in the model. The vertical profile of NO_2 calculated by the model is dependent on the vertical profile of aerosol surface area assumed, since NO_2 concentrations are reduced by the heterogeneous hydrolysis of N_2O_5. When the heterogeneous hydrolysis of N_2O_5 is neglected, predicted BrO slant columns are reduced by a factor of 2. However, the reduction in NO_2 concentrations due to heterogeneous reactions on sulphate aerosol saturates fairly readily, that is, when the aerosol surface area exceeds a certain threshold, a further increase in aerosol surface area has little effect on NO_2 concentrations [Mills et al., 1993]. The sulphate aerosol surface area taken from observations and used in the model is significantly greater than this saturation threshold. Consequently, the BrO slant columns are insensitive to the aerosol profile assumed, provided the aerosol surface area in the atmosphere during the winter of 1993-1994 also exceeded this threshold. Once the reaction of N_2O_5 with HNO_3 is saturated, NO_2 abundances are controlled only by the exposure of the air to sunlight. Since BrO slant columns are anticorrelated with NO_2 concentrations, BrO slant columns should increase with latitude and exhibit a significant annual cycle, peaking at the winter solstice.

The dependence of BrO slant columns on the vertical profile of Br_y was investigated using the one-dimensional model, by constraining the vertical profile of Br_y to increase linearly from 0 pptv at 10 km to 15 pptv at 20 km and above, and alternatively by constraining the vertical profile of Br_y to increase linearly from 0 pptv at 14 km to 15 pptv at 24 km. The resulting variations of BrO slant column with SZA through sunset are shown in Figure 10. An increase in the amount of BrO in the lower stratosphere is seen to increase the BrO slant columns between 80° and 90° SZA by similar amounts. When the spectra are analyzed using a reference spectrum measured at 80° SZA, the resulting differences in BrO slant column are insensitive to the altitude of the lower edge in the Br_y profile.

The only remaining variable which influences BrO slant columns is the amount of Br_y in the stratosphere. As mentioned earlier, the sunset observations of BrO are
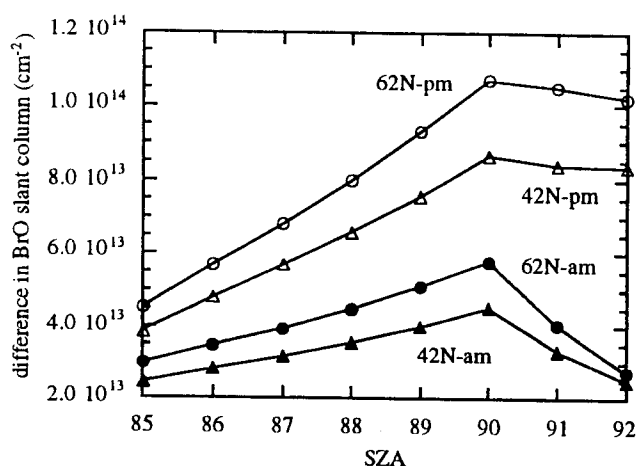
Figure 11.   BrO slant columns predicted by the one-dimensional model for air from 42°N and 62°N.

consistent with 21 ± 3 pptv of Br_y in the stratosphere. When comparing this with Arpag et al.'s [1994] estimation of 5 pptv of BrO above 12 km, two facts should be borne in mind. First, the above estimate is of the total inorganic bromine content, or Br_y, whereas Arpag et al. estimated the profile of BrO. The vertical profile of BrO which corresponds to this Br_y profile is discussed below. Second, Arpag et al.'s BrO profile is almost certainly incorrect as a result of their attempt to fit model results which neglected the rapid diurnal variation of BrO to their observations.

5.3. Variability of BrO Slant Columns

Slant columns of BrO are expected to vary from day to day, by analogy with the variation of vertical columns of O_3, as a result of vertical and horizontal air motion. At midlatitudes, the height of the tropopause varies considerably from day to day. During the European Arctic Stratospheric Ozone Experiment (EASOE), the height of the tropopause at Esrange (68°N) was observed to vary between 7 and 14 km [Naujokat et al., 1992]. The one-dimensional model was thus used to investigate the sensitivity of BrO slant columns to a ± 3.5-km displacement of the mixing ratios of all model constituents. The air motion was assumed to be adiabatic, thus the air temperature was reduced by 10 K for every kilometer of ascent. Vertical air motion was found to change the absolute BrO slant columns but to have little effect on the difference in BrO slant column between 80° and 90° SZA.

Latitudinal air motion will also affect BrO slant columns. Air which has spent most of its time at higher latitudes will contain less NO_2 than air which has been exposed to more sunlight at lower latitudes. Since sunset BrO abundances are inversely related to NO_2 abundances, air from higher latitudes should have larger BrO slant columns than air from lower latitudes. The effect of latitudinal NO_2 gradients was tested by running the one-dimensional model at 42°N and 62°N, that is, 10° latitude either side of Cambridge. As shown in Figure 11, latitudinal air motion can cause BrO slant columns to vary by approximately 20%.

Changes in stratospheric temperature also cause BrO slant columns to vary, since the rate of the termolecular reaction forming $BrONO_2$ has a significant, negative temperature dependence. When the stratosphere is cold, $BrONO_2$ is
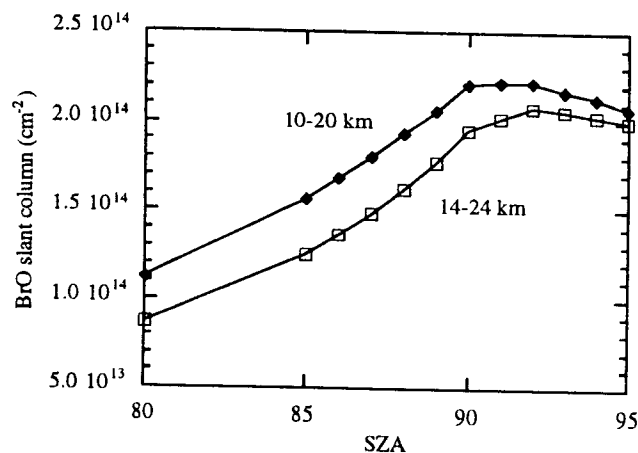

Figure 10.   The variation of BrO slant column through sunset for vertical profiles of BrO increasing from 0 to 15 pptv between 10 and 20 and between 14 and 24 km.

formed rapidly and less BrCl is formed. This causes BrO slant columns at both sunrise and sunset to be smaller. BrO slant columns were calculated to vary by 25% over the range of temperatures experienced.

Tropospheric BrO would also contribute to the observed BrO slant columns and is a potential contributor to the observed variability. BrO concentrations ranging from < 4 pptv to 17 pptv have been measured in the Arctic boundary layer [*Hausmann and Platt*, 1994]. Several marine processes have been proposed to explain the production of BrO during Arctic springtime, including heterogeneous reactions on sea salt aerosol or sea ice. BrO concentrations are expected to be smaller at midlatitudes, particularly in continental air masses such as those above Fritz Peak, Colorado, where a similar day-to-day variability in BrO slant columns was observed [*Arpag et al.*, 1994]. Overall, it seems unlikely that tropospheric BrO is responsible for the observed variability in BrO, particularly since the technique is least sensitive to tropospheric absorbers.

6. Vertical Profile of BrO: Comparison with In Situ Measurements

As described earlier, measured BrO slant columns are consistent with model predictions which assume that the stratospheric vertical profile of Br_y increases from 0 pptv at 14 km to 21 pptv at 24 km and above. Since the model reproduces the variation of BrO slant column with SZA reasonably well, it is constructive to compare the corresponding vertical profile of BrO with in situ measurements of BrO abundances. The vertical profiles of BrO predicted by the model at 80° and 85° SZA at sunrise are shown in Figure 12, together with the in situ BrO mixing ratios measured by *Brune et al.* [1988] between 37° and 61°N over North America. The figure shows that when the abundance of Br_y is constrained at 21 pptv by the measured BrO slant columns, the vertical profiles of BrO predicted by the model are consistent with in situ measurements of BrO. Note that the measurements provide most information about the amount of Br_y in the low stratosphere and are insensitive to the amount of Br_y above 35 km.
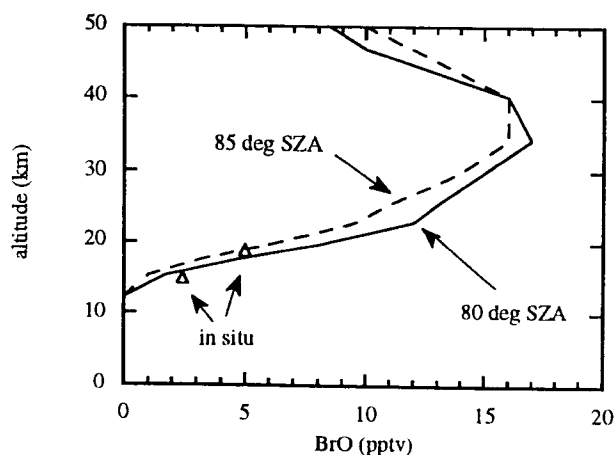

Figure 12. The vertical profiles of BrO predicted by the model at 80° and 85° SZA. The model is constrained by the slant column measurements to have 21 pptv of Br_y in the stratosphere. Also shown are BrO mixing ratios determined by the in situ measurements of *Brune et al.* [1988].

7. Conclusions

The agreement between the measured BrO slant columns and model predictions has been markedly improved by consideration of the two-dimensional variation of BrO abundances across the region of atmosphere traversed by the light from the sun, and by the inclusion of recent laboratory data on the absorption cross section of $BrONO_2$. The effects of heterogeneous reactions involving bromine have been considered and shown to cause BrO slant columns predicted by the model at sunrise to be slightly reduced. Measured BrO slant columns at sunrise are in best agreement with model predictions which neglect the heterogeneous hydrolysis of $BrONO_2$.

The observations of BrO slant columns at sunset are consistent with 21 ± 3 pptv of inorganic bromine in the stratosphere. This conclusion is unaffected by reasonable changes to the aerosol surface area assumed in the model, because the heterogeneous hydrolysis of N_2O_5 is saturated. The use of a daily reference spectrum measured at 80° SZA each twilight makes the measurements insensitive to the altitude of the lower edge in the vertical profile of Br_y. BrO slant columns predicted at sunrise are highly sensitive to small changes in the absorption cross section of $BrONO_2$. The large variability of BrO slant columns measured on different days can be partially explained by the meridional advection of air and changes in stratospheric temperature. Tropospheric BrO could contribute to the observed variability and further work is needed to eliminate this possibility.

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