



Tropospheric and stratospheric BrO columns over Arrival Heights, Antarctica, 2002

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[1] Spectroscopic measurements of BrO using direct sun and zenith sky viewing geometries are combined in an optimal estimation retrieval algorithm to obtain tropospheric and stratospheric columns of BrO. Twenty-two twilight periods are investigated over Arrival Heights, Antarctica (77.8°S, 166.7°E) during the polar spring period of 2002. This paper presents the first tropospheric and stratospheric BrO column retrievals from UV-visible ground-based measurements for a polar location. A direct comparison is made between stratospheric columns retrieved at 80°, 84°, and 88° solar zenith angles (SZA) from the spectroscopic measurements and those calculated by the SLIMCAT three-dimensional chemical transport model. The ground-based column BrO observations are consistent with a SLIMCAT stratospheric Br_y loading of 21.2 parts per trillion at 20 km. SLIMCAT reproduces the observed sunrise column BrO increase but does not match the sunset observations, which display less variation. The significant warming of the Antarctic polar stratosphere in 2002 led to highly variable stratospheric columns being observed. The observed column BrO decreased with the transition from vortex to extravortex air on 21 September but did not change much following the return of the vortex on 12 October. For the tropospheric column, an almost normal distribution consistent with a “background” of $0.3 \pm 0.3 \times 10^{13}$ molecules cm⁻² is observed from the ground (80°, 84°, and 88° for both sunrise and sunset). A statistically significant “bromine explosion” event (at the 2σ level) was detected at the end of October with a tropospheric column of $1.8 \pm 0.1 \times 10^{13}$ molecules cm⁻². The measured tropospheric columns are compared with the tropospheric Model of Atmospheric Transport and Chemistry–Max Planck Institute for Chemistry version model. The tropospheric BrO sunrise column observations can only be explained with an additional bromine source other than decomposition of CH₃Br and downward transport of long-lived bromine from the stratosphere. A comparison with the spaceborne Global Ozone Monitoring Experiment (GOME) found the total columns observed from the ground to be 16–25% smaller than the total columns observed by GOME for SZAs between 80° and 88°.

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1. Introduction

[2] In the stratosphere catalytic ozone destruction cycles involving bromine are thought to account for ~40% of the ozone loss over Antarctica [Lee *et al.*, 2002]. While this ozone loss is limited by the heterogeneous release of chlorine from its reservoir species on polar stratospheric clouds (PSCs), bromine continues to destroy ozone in the absence of PSCs via the hydrolysis of BrONO₂ on cold stratospheric aerosol [Solomon, 1999; Danilin *et al.*, 1996; Lee *et al.*, 2002]. At midlatitudes between 30–60°S catalytic ozone destruction involving bromine accounts for about a quarter of the observed ozone losses during winter and spring [Lee *et al.*, 2002].

[3] The polar spring of 2002 in the Antarctic was an unusual year with the polar vortex splitting in two and the remaining vortex becoming weaker, resulting in reduced

stratospheric ozone loss relative to previous years [Hoppel *et al.*, 2003; Allen *et al.*, 2003]. The early polar vortex split due to the unprecedented stratospheric warming provided a unique opportunity to study air masses both inside and outside the polar vortex from the ground at Arrival Heights (77.8°S, 166.7°E) early in the polar spring.

[4] Long-lived bromine source gases account for a stratospheric bromine loading of ~ 15 parts per trillion by volume (pptv) [World Meteorological Organization (WMO), 2003]. Combined observational and chemical modeling studies from 1995 to present indicate that the stratospheric bromine loading is between 18 ± 3 and 21.5 ± 3 pptv [Fish *et al.*, 1995; Pfeilsticker *et al.*, 2000; Sinnhuber *et al.*, 2002, 2005; Schofield *et al.*, 2004b; Salawitch *et al.*, 2005]. Transport of short-lived tropospheric bromine species to the stratosphere is required to be included within models to explain this shortfall in the total stratospheric bromine budget.

[5] In the polar regions the role of BrO causing almost complete boundary layer ozone loss has been well documented in the Arctic [Barrie *et al.*, 1988; Bottenheim *et al.*, 1990; Solberg *et al.*, 1996; Tuckermann *et al.*, 1997; Miller *et al.*, 1997; Oltmans *et al.*, 1998] and Antarctic [Kreher *et al.*, 1997; Frieß *et al.*, 2005]. The linkage of these high-BrO events and increased mercury deposition (thus increased mercury levels in the polar biosphere) has major health implications for the polar regions [Schroeder and Munthe, 1998]. The exact mechanism for the release of bromine is currently not fully understood. Proposed mechanisms include the autocatalytic release of bromine from sea salt either from accumulation on the snowpack over the polar winter with subsequent snow processing [Tang and McConnell, 1996], or from sea salt aerosol processing [Simpson *et al.*, 2005]. There is increasing evidence for the involvement of frost flowers [Kaleschke *et al.*, 2004], however, the exact role of open leads and frost flower involvement in the process is unknown [Simpson *et al.*, 2005].

[6] The ability to differentiate tropospheric and stratospheric trace gas species is vital because of the very different processes that occur in these regions, and this is especially true for BrO in the polar regions. The Umkehr method of retrieving the vertical distribution of ozone from ground-based spectroscopy was originally described by Mateer and Duetsch [1964] and Ramanathan and Dave [1957] and more recently applied in advanced retrievals [e.g., Petropavlovskikh *et al.*, 2005]. A similar technique using observations at different sun angles for ground-based stratospheric profiling was pioneered by Brewer *et al.* [1973], Noxon [1975], and McKenzie *et al.* [1991] for NO₂. Recent work by Preston *et al.* [1997] and Hendrick *et al.* [2004] have implemented the formal optimal estimation method of Rodgers [2000] in stratospheric profile retrievals of NO₂ from ground-based zenith sky spectroscopy. Tropospheric and stratospheric BrO column retrievals have been performed by Schofield *et al.* [2004a] for the midlatitude site of Lauder, New Zealand. BrO in the boundary layer has been retrieved using MAXDOAS with a geometric interpretation by Hönninger and Platt [2002]. The use of O₄ to constrain the tropospheric path will enable more accurate boundary layer profiling from MAXDOAS in the future [Wagner *et al.*, 2004; Sinreich *et al.*, 2005]. This paper presents the first tropospheric and stratospheric BrO

column retrieval from UV-visible ground-based measurements for a polar location.

2. Ground-Based Spectroscopic Measurements

[7] Spectroscopic measurements are made at Arrival Heights, Antarctica (77.8°S, 166.7°E) located at an altitude of 185 m above the sea ice on Ross Island, at the edge of the Ross Sea ice shelf. Arrival Heights is one of the primary measurement sites that makes up the Network for the Detection of Stratospheric Change (NDSC), now the Network for the Detection of Atmospheric Composition Change (NDACC).

2.1. Instrumentation

[8] Zenith sky measurements were made with an Acton SpectraPro-500 spectrometer (a commercial Czerny Turner monochromator), with a focal length of 500 mm, an aperture ratio of $f/6.9$ and a field of view of 7°. The detector was a photo diode array cooled to -50°C . The 1200 grooves mm^{-1} grating provides a wavelength coverage of 332–371 nm at a resolution of 0.58 nm and full width half maximum (FWHM) of 15.5 pixels. A detailed description of the spectrometer and nonlinear least squares differential optical absorption spectroscopy (DOAS) method used to derive the zenith sky differential slant column densities (DSCDs) is given by Kreher *et al.* [1997]. Zenith sky measurements were made up to 95° solar zenith angles (SZA) because of the slow change in SZA at this polar latitude. The resultant longer integration times increased the signal to noise, and thus reduced the measurement errors.

[9] The direct sun viewing spectrometer was an Acton 275 (a commercial Czerny Turner spectrometer with spherical mirrors). The detector was a Hamamatsu back thinned charge coupled device (CCD) module with 1044 3.2 mm \times 0.024 mm pixels. The detector was cooled to -20°C . The 1200 grooves mm^{-1} grating provides a wavelength coverage of 324–395 nm at a resolution of 0.5 nm and FWHM sampling of about 7 pixels. A complete instrument description and DSCD DOAS derivation is given by Schofield *et al.* [2004b]. The low horizon surrounding the Arrival Heights site allowed direct sun measurements to be made up to 89° SZA.

2.2. DOAS Analysis

[10] DSCD values from both direct sun and zenith sky viewing spectroscopic measurements were evaluated using the well-known DOAS technique (for a review of DOAS see Platt [1994]). A ratio of twilight radiance spectra with respect to a noon reference spectrum removes the complicating Fraunhofer lines present in solar radiance measurements. In both the direct sun and zenith sky geometries noon reference spectra were chosen for each day (as close as possible to the local noon, yet still under cloud-free conditions). The range of SZAs sampled by the DSCDs differed between measurement days because of clouds, solar elevation and the topography. The broadband absorption features and the Rayleigh and Mie scattering features that make up the spectral background baseline were removed by fitting low-order polynomials (high-pass filter). A nonlinear least squares fitting procedure was then employed to fit differential cross sections for each absorber, thus determining

their respective absorptions [Aliwell *et al.*, 2002]. The cross sections of O₄ [Greenblatt *et al.*, 1990], O₃ [Voigt *et al.*, 2001] (203 K and 280 K), NO₂ [Harder *et al.*, 1997], OClO [Kromminga *et al.*, 2003], BrO [Wilmouth *et al.*, 1999], Ring (measured) [Fish and Jones, 1995; Solomon *et al.*, 1987] and CH₂O [Meller and Moortgat, 2000] were fitted to the logarithm of the spectral ratio of the twilight to noon radiances. For the zenith sky DSCDs a fitting window of 344.5–358.5 nm was used. The direct sun DSCDs used a fitting window of 345.8–359.8 nm.

2.3. Measurement Covariance

[11] The covariance matrix of the uncertainties in the measurements S_e was constructed by placing the variance arising from one standard deviation of the error from the DOAS spectral fitting along the diagonal of the matrix. The off-diagonal elements are assumed to be zero. The measurement error covariance matrix derived from the DOAS fitting is assumed to incorporate all the errors that are present in determining the DSCDs.

2.4. Column Retrievals

[12] The methodology for retrieving tropospheric and stratospheric columns at a number of SZAs by combining direct sun and zenith sky measurements is described in detail by Schofield *et al.* [2004a]. In brief: the direct sun DSCDs and the zenith sky DSCDs are combined to create the measurement vector \mathbf{y} . A radiative transfer model (forward model) calculates the DSCDs for a given series of BrO profiles at different SZA; this is the state vector \mathbf{x} . Each element of the matrix of BrO profiles is perturbed and the resultant change in the calculated DSCDs is used to construct the Jacobian or weighting function matrix \mathbf{K} . Optimal estimation [Rodgers, 2000] is the technique used to invert the measurements \mathbf{y} to give the retrieved state $\hat{\mathbf{x}}$. The prior knowledge of the state \mathbf{x}_a , its covariance \mathbf{S}_a , the measurements \mathbf{y} and their covariance \mathbf{S}_e are all included in the inversion to give the solution which is optimal given the constraints of the measurements and a priori knowledge. The equation that is solved for the linear problem is

$$\hat{\mathbf{x}} = \mathbf{x}_a + \mathbf{S}_a \mathbf{K}^T (\mathbf{K} \mathbf{S}_a \mathbf{K}^T + \mathbf{S}_e)^{-1} (\mathbf{y} - \mathbf{K} \mathbf{x}_a) \quad (1)$$

Stratospheric and tropospheric columns are then derived at each SZA by integrating the appropriate altitude range of $\hat{\mathbf{x}}$.

2.4.1. Forward Model

[13] The calculation of the DSCDs for a given set of BrO profiles is conducted by a radiative transfer algorithm. The radiative transfer algorithm is defined with spherical coordinates from 0 to 70 km in discrete atmospheric layers. The effects of refraction, molecular absorption, Rayleigh and Mie scattering were included. Only first-order scattering is included, since multiple scattering is negligible for the DSCDs of BrO for SZA < 92° [Sinnhuber *et al.*, 2002; Hendrick *et al.*, 2006]. The radiative transfer model (forward model) parameters of ozone, temperature and pressure describing the climatology were provided by ozonesonde measurements conducted at McMurdo (4 km from Arrival Heights). The aerosol extinction profile was derived from lidar measurements at McMurdo. For the troposphere, an aerosol extinction profile from the winter climatology of Lauder was assumed (J. B. Liley, personal communication,

2003), derived from backscatter sondes. The NO₂ profile was obtained from SAGE II measurements made on 7 October 2002 for Arrival Heights. The forward model parameters were all found to produce negligible errors in the final retrieved values [Schofield, 2003] (see also section 2.4.4). The date 7 October was chosen and these profiles were held constant for all of the retrievals.

[14] A tropopause height of 8.8 km was used for all of the polar column retrievals. This height was derived by considering all of the ozonesonde data (8 flights) available for the spring period of 2002. The effect of different tropopause heights is discussed in section 4.2.

2.4.2. State Vector, A Priori, and A Priori Covariance

[15] The diurnal variation of the vertical distribution of trace gas species of NO₂ and BrO adds complication to the retrieval problem. This has been addressed by Preston [1995] and Hendrick *et al.* [2004] by incorporating a photochemical model in the forward modeling of the inversion problem. Schofield *et al.* [2004a, 2004b] simultaneously retrieve the diurnal change in the trace gas distribution directly from the measurements.

[16] Similar to the tropospheric and stratospheric column retrievals performed for the midlatitude site, Lauder [Schofield *et al.*, 2004b], the state vector is composed of BrO profiles at different diurnal stages to account for the strong diurnal variation of BrO. The state vector is constructed from the seven profiles at SZAs of 0°, 80°, 84°, 88°, 90°, 92° and 97°, with each profile from 0 to 70 km in steps of 1 km, thus $\hat{\mathbf{x}}$ is a vector of length 7 × 71 (with the profiles stacked in ascending order of SZA).

[17] A stationary chemical box model was used to determine the stratospheric a priori set of profiles using SLIMCAT [Chipperfield, 1999] chemistry with the most recent update of reaction rates [Sander *et al.*, 2003]. Unlike the midlatitude case where there is a clear decrease in the VCD from 80° SZA, the slower rate of change of SZA in the polar scenario means that seven profiles can be chosen to describe the diurnal change (0°, 80°, 84°, 88°, 90°, 92° and 97° SZA) with the model predicting a decrease in the VCD to occur after 90° for the sunset on 7 October. There is almost no diurnal variation between the 80° and 90° stratospheric profiles. There is however, a rapid decrease in the BrO VCD from 90° to 92°, with almost no BrO present at 97°. Figure 1 shows the a priori profile diurnal variation for Arrival Heights in the spring used for the column retrievals in this work. The a priori 0° tropospheric profile used is based on a winter balloon BrO observation made at Kiruna [Fitzenberger *et al.*, 2000]. The a priori noon profile is assumed to have a peak at $\sim 1 \times 10^{13}$ molecules cm⁻³ at 3 km and decreasing to zero at the tropopause. For the other tropospheric a priori profiles a diurnal decrease similar to the diurnal decrease in the stratosphere was assumed. These tropospheric a priori assumptions are discussed in section 4.2.

[18] An a priori error of 30% of the peak value was assumed in the construction of \mathbf{S}_a . The a priori covariance of the Lauder data set [Schofield *et al.*, 2004b] was 50%. The smaller a priori error (larger constraint) was required because of the smaller SZA range of the Arrival Heights measurements, especially at the beginning of the measurement period. The 30% error was sufficient to provide a good

