# Comparison of ground based measurements and model calculations of bromine monoxide in Nairobi (1S, 36E)

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## Introduction

Bromine species have discovered to play an important role in ozone depletion in the stratosphere. Stratospheric inorganic bromine was estimated in 1999 to be 18-21 ppt from organic precursor measurements and from coincident measurements of bromine monoxide (BrO). Its contribution to total stratospheric ozone loss is estimated at about 25%. In contrast to chlorine concentrations which have stabilized as a result of the Montreal Protocol, the maximum of bromine source gas emissions have not yet reached. Measurements of BrO are reported in various studies for high and middle latitudes but there are no long term and only a few campaign measurements in low latitude regions and in particular in Africa. To improve on this situation, a permanent DOAS measurement station was set-up in 2002 in Nairobi (1°S, 36°E) as part of the BRemian DOAS (Differential Optical Absorption Spectroscopy) network of atmospheric Measurements (BREDOM).
Measurements of BrO in the tropics are special because of the expected absence of seasonality as result of the small variations of the $NO_2$ values during the year and the smaller impact of horizontal transport. As result of the high tropopause, the BrO columns are also expected to be generally smaller than in mid and high latitudes.
To test our current understanding of bromine chemistry, the measurements are compared with calculations of BrO slant column densities from a 1D photochemical stacked box model which is based on the photochemical scheme from *[Chipperfield, 1999]*, coupled with a radiative transfer model *[Rozanov et al., 2001]* to allow direct comparisons between the observed and modelled data. The comparison provides an important low-latitude extension of the model-measurement comparisons reported in *[Sinnhuber et al.2002].*

## Experimental Setup

- Czerny-Turner Spectrograph L.O.T. MS257 (focal length 257 mm, 1200 l/mm grating) and CCD Andor DV440-BU (2048 x 512 pixels) for the UV spectral range
- L.O.T. MS260i(focal length 260 mm, 600 l/mm grating) and CCD Andor DV420-BU (1024 x 256 pixels) for the visible range
- UV/vis wavelength regions: 320 – 410 nm, 395 - 565 nm
- spectral resolution: ~0.5 nm
- targeted trace gases: $O_3$, $NO_2$, BrO, HCHO, IO, OClO
- atmospheric viewing: continuous alternating observations between zenith and horizon (4 off axis viewing directions: 4°, 7°, 16°, 30°), achieved by employing a mirror on a turntable moved by a computer controlled servomotor as shown in Figure 1
- daily calibration measurements

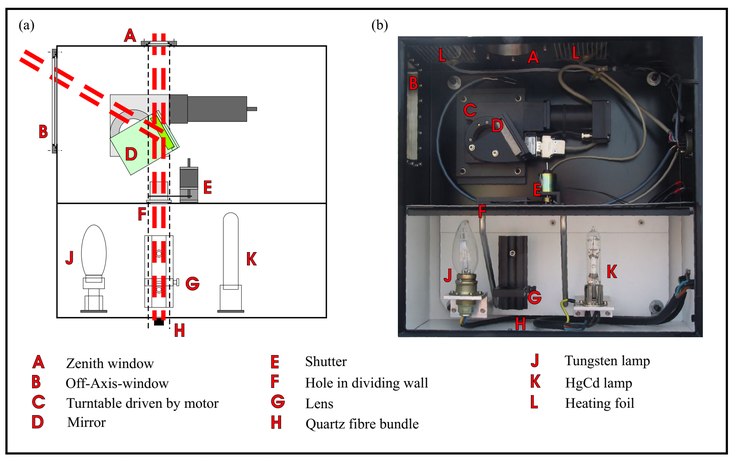


**Figure 1:** Setup of the telescope.

## Measurements

For the analysis of the measured spectra the Differential Optical Absorption Spectroscopy (DOAS) method is applied:

- fitting window from 344.7 nm to 359.0 nm
- cross sections $NO_2$, $O_3$ (221 K, 241 K), $O_4$, HCHO, BrO and Ring

To obtain the DSCDs the average of the slant columns in the solar zenith angle (SZA) range from 89° to 92° is calculated and then the reference slant column at 80° (+/- 2°) is subtracted. The accuracy of the measurements is estimated to about 20%.

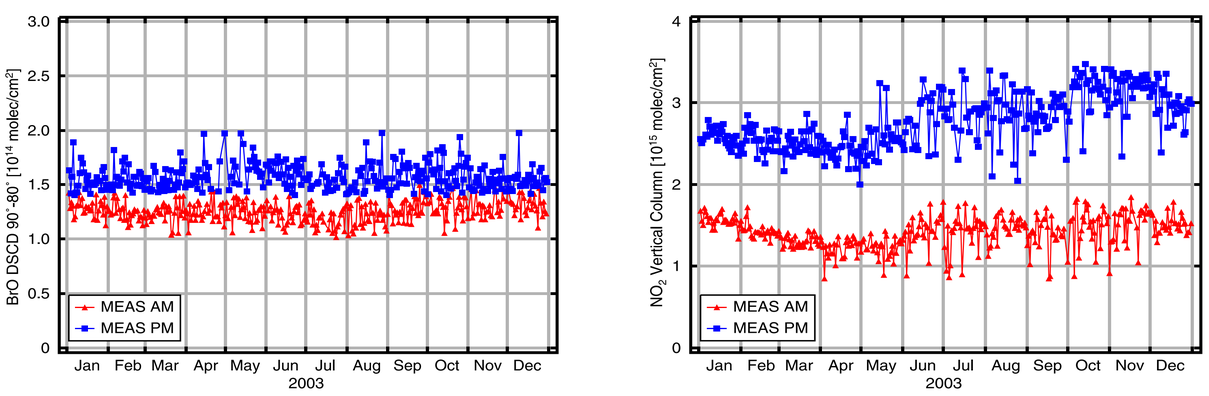


**Figure 1:** The left picture show observations of BrO above Nairobi, 2003. Shown are differential slant columns between solar zenith angles of 90° and 80°. In the right picture $NO_2$ vertical columns above Nairobi observed at solar zenith angles around 90° are presented. Morning and afternoon values are given.

The results of the BrO DSCDs over Nairobi for the year 2003 are presented in figure 2. It can be seen that the afternoon values are slightly higher than the morning values which implies that BrO is released from $BrONO_2$ during the day and during the night the BrO is stored in its reservoir HOBr. The seasonal variation of BrO is most likely controlled by the seasonal variation of $NO_2$ and the following formation of the reservoir $BrONO_2$. As shown in figure 2, no strong seasonal variation of $NO_2$ is observed over Nairobi which is in agreement with the BrO measurements that also vary only slightly. The absolute values of the BrO DSCD are about $1.5x10^{14}$ molecules/cm$^2$ for the evening and about $1.3x10^{14}$ molecules/cm$^2$ for the morning which is in the same order of magnitude as for measurements at mid- and high latitude sites*[e.g. Richter et al., 1999]*.

## Comparison with model results

The model is a 1D photochemical stacked box model which is based on the photochemical scheme from SLIMCAT *[Chipperfield et al., 1999]*. It contains a comprehensive description of stratospheric $O_x$, $NO_x$, $ClO_x$, $BrO_x$, $HO_x$ and $CH_yO_x$ oxidation chemistry. The model was initiated with the output of a global 2D chemistry transport and photochemistry model.

Model details:

- photochemical reaction rate constants and photolysis cross-sections from the NASA/JPL compilation 2002
- 21 levels ranging from about 870 to 0.02 HPa (an altitude range from about 2 to 80 km)
- all of the species in the model were integrated separately using a 5 minute time step
- series of model experiments at the 15$^{th}$ of every month at latitude of 1.27°S were performed
- two runs with different meteorological input data were made, one using climatological and the other ECMWF data for the year 2003
- third run using the ECMWF data includes the reaction $BrONO_2 + O(^3P)$ ->> $BrO + NO_3$.

To calculate BrO slant column densities from the modelled BrO the radiative transfer model SCIATRAN is used. The calculations were made for a wavelength of 350 nm, the centre wavelength of the fitting window.

An example of calculated BrO slant columns from the model and measurements for August 15$^{th}$ 2003 is shown in figure 3. The slant columns from the model run show no significant difference when the climatological or the ECMWF data are used in the calculation. As investigated by *Soller et al.[2001]* the reaction of $BrONO_2$ with $O(^3P)$ could be an important loss of bromine nitrate in the stratosphere with increasing concentrations of BrO during daytime. Due to the low concentrations of $O(^3P)$ the influence is small in the lower stratosphere but dramatically increases above an altitude of 20 km. If the reaction $BrONO_2 + O(^3P)$ ->> $BrO + NO_3$ is included in the calculation the values of the slant columns increases by about 20% in the morning and by about 10% in the evening.

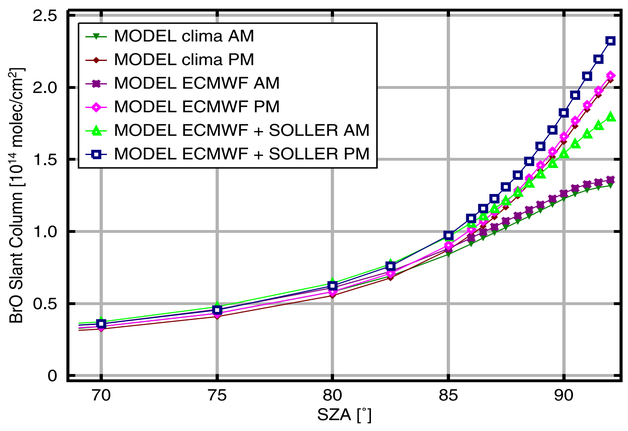


**Figure 3:** Modelled BrO slant columns for Nairobi, August 15$^{th}$ 2003.

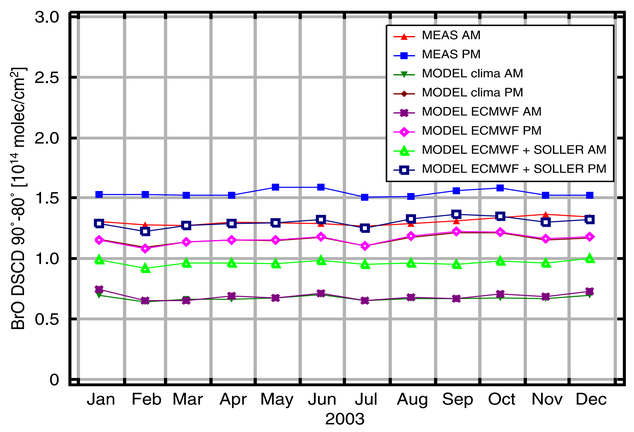


**Figure 4:** Comparison of observed and modelled BrO Differential Slant Column Densities for the year 2003. For the observations the monthly mean is presented.

Figure 4 shows DSCDs for all months for the different model runs in comparison with the measurements. For the measurements the monthly mean is presented. The seasonal and the diurnal variation is well captured by the model. However, the observed BrO DSCDs are higher than the DSCDs for the runs with climatological or ECMWF data by about $4x10^{13}$ molecules/cm$^2$ (25%) in the evening and $6x10^{13}$ molecules/cm$^2$ (45%) in the morning. By introducing the reaction $BrONO_2 + O(^3P)$ ->> $BrO + NO_3$ in the model runs the difference decreases to values of about $2x10^{-13}$ molecules/cm$^2$ (15%) in the evening and $3x10^{13}$ molecules/cm$^2$ (20%) in the morning. These values are within the combined uncertainties of model and measurements.

## Conclusions

To test our understanding of bromine chemistry in tropical regions one year of ground-based measurements were compared with results from a chemical stacked box model:

- measured differential slant columns (90° - 80° SZA) show only little seasonal variation which is related to the small seasonal variation of $Br_y$ and the lack of a seasonality of $NO_2$
- clear diurnal variation of BrO, the average BrO DSCD being $1.3x10^{14}$ molecules/cm$^2$ in the morning and $1.5x10^{14}$ molecules/cm$^2$ in the evening
- measured DSCDs show generally good agreement with values calculated by the model, the diurnal variation and the lack of seasonality are well reproduced
- agreement between model and measurement can be further improved to be within the combined uncertainties by including the reaction $BrONO_2 + O(^3P)$ *[Soller et al., 2001]*

The good agreement between model and observations are in agreement with the results of *Sinnhuber et al. [2002]* indicating that our current models of the mechanisms controlling the stratospheric BrO are also valid for the tropical region.

## Selected References

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