Modeling of BrO Slant Columns over Bremen (53°N)

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1 Introduction

The DOAS-technique (Differential Optical Absorption Spectroscopy) for detecting various trace gases is used at the Institute of Environmental Physics (University of Bremen) since 1993. We maintain stations in high [1] and mid latitudes [2]. DOAS-measurements yield differential slant column densities (DSCD) by subtracting the slant column density (SCD) determined by the reference spectrum from the SCD determined by the actual spectrum. A slant column is the sum of all molecules of a trace gas along the observed light path. The reference spectrum is measured at the smallest solar zenith angle (SZA). To interpret measured DSCD's of shortlived species like BrO it is important to compare them to photochemical model calculations because of the rapid changes in the concentrations during twilight. Previous studies have shown inconsistencies between inside and outside vortex bromine demonstrated in [3]. This work deals with heterogeneous chemistry and NO_x budgets in mid-latitudes mostly.

2 The model package SLACO

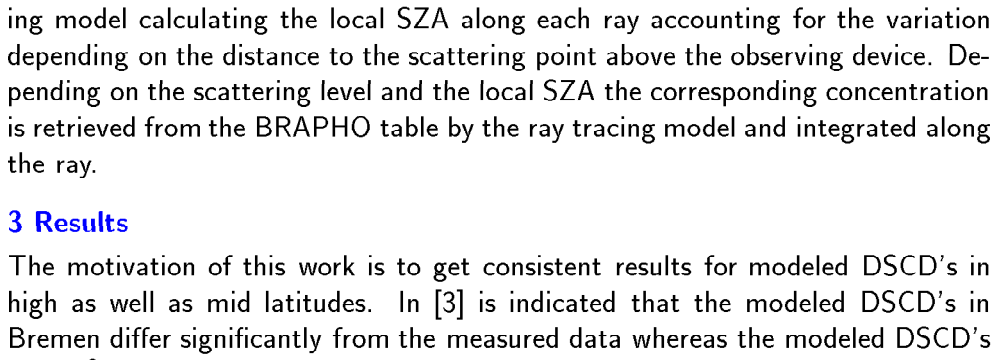
The model package SLACO [4] consists of different modules including the stacked 1-D photochemical box trajectory model BRAPHO and a ray-tracing-model [5]. BRAPHO [6] simulates the diurnal variation of shortlived species like BrO in form of a table containing the concentrations for different heights and SZA's.
Each level in the BRAPHO table represents a scattering level in the ray tracing model calculating the local SZA along each ray accounting for the variation depending on the distance to the scattering point above the observing device. Depending on the scattering level and the local SZA the corresponding concentration is retrieved from the BRAPHO table by the ray tracing model and integrated along the ray.

3 Results

The motivation of this work is to get consistent results for modeled DSCD's in high as well as mid latitudes. In [3] is indicated that the modeled DSCD's in Bremen differ significantly from the measured data whereas the modeled DSCD's in Ny-Ålesund represent the measured data quite well. The same standard photochemistry is used in both cases. The standard chemistry is based on [7] and includes HOBr cross sections taken from [8]. The standard photochemistry achieved good agreement between modeled and measured DSCD's in Bremen in the afternoon but in the morning the modeled DSCD's are too small by roughly 25% (see Fig. 1).
To solve the discrepancy inside the model the photochemistry was varied extensively in preceding work [3]. The set of altered parameters includes $BrONO_2$ cross sections taken from [9] multiplied with factors of 1.4 to 2 and reduction of $BrONO_2$ production rate constants. These parameters were altered with respect to the uncertainties given by [7] derived from all known measurements. The described variations were applied to different vortex scenarios including high latitude scenarios inside and outside vortex, and mid latitude outside vortex scenario. This study was done to point out that there are more parameters responsible for the increase of the BrO DSCD's than the ones specified in [3].

(i) More NO_x in the middle stratosphere

Figure. 1: Modeled DSCD's for BrO over Bremen (16.3.1997)



Left: measured DSCD's are compared to different modeled DSCD's including standard chemistry (red curve) and varied NO_x profiles (green curve). HALOE data were used to vary the initial SLIMCAT NO_x profiles.
Right: The HALOE NO_2 profile (red curve) measured at 90.3° SZA AM is compared to the modeled NO_2 profiles at 90.0° SZA AM (green curve) and 92.0° SZA AM (blue curve).

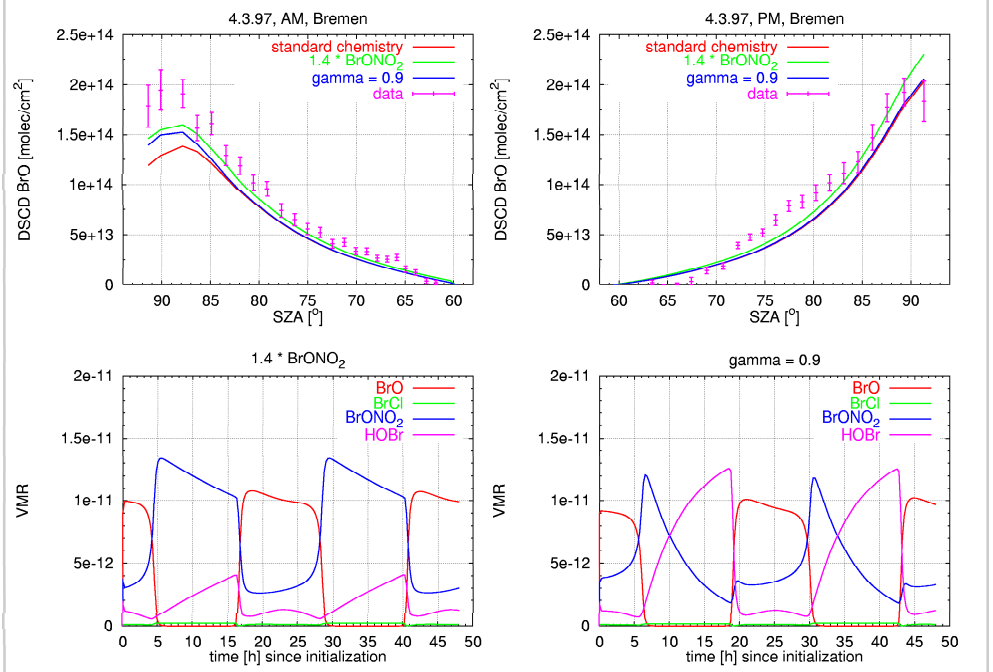
The motivation for this study was the analysis of the interconnection of the bromine and the NO_x chemistry. Further we wanted to get some knowledge about the magnitude of the influence of NO_x profiles on the BrO DSCD's. The upper two plots of Fig. 2 show the modeled DSCD's initialized with NO_x data measured by HALOE (HALogen Occultation Experiment flying on the Upper Atmosphere Research Satellite - UARS) [9] compared to measured data and modeled DSCD's initialized with standard chemistry and SLIMCAT data for NO_x. These two plots show that the modeled DSCD's initialized with HALOE NO_x data are smaller from 86° to 92° SZA compared to standard chemistry. This is because of the increased NO_2 values around 20 to 30 km as can be seen in the lower two plots of Fig. 2. The increased NO_2 values lead to an enhanced production of $BrONO_2$ especially during twilight when the chemical equilibrium is being shifted to BrO.

These findings indicate that the values of the BrO DSCD's are heading in the wrong direction if the NO_x below 30 km is increased.

(ii) Uptake Coefficient of the $BrONO_2$ Hydrolysis

In this study the uptake coefficient of the $BrONO_2$ hydrolysis was changed. In particular it was set to a static value of 0.9 for this model run. Normally BRAPHO calculates the uptake coefficient by a heterogeneous chemistry module developed by Ken Carslaw (MPI for chemistry in Mainz). This study was done to analyze the influence of the heterogeneous chemistry on the BrO DSCD's in mid latitudes.

Figure. 2: Modeled DSCD's for BrO over Bremen (4.3.1997)



Above: measured DSCD's are compared to different modeled DSCD's including standard chemistry (red curve). The model runs differ in $BrONO_2$ cross sections (green curve) and in the uptake coefficient for the $BrONO_2$ hydrolysis (blue curve).
Below: Partitioning of bromine species of the the model runs '1.4 * $BrONO_2$' and 'gamma = 0.9' are compared. Please notice that time = 0 corresponds to 12:00 local time because the model is initialized with SLIMCAT data at 12:00 noon.

Fig. 1 shows that the model run with the increased uptake coefficient leads to larger AM-DSCD's compared to the model run with increased $BrONO_2$ cross sections. Whereas the PM-DSCD's are almost unaffected by the increased uptake coefficient. This is because of the fast conversion of $BrONO_2$ to HOBr (see Fig. 1 below right) during nighttime and subsequent photolysis during twilight producing more BrO.

4 Conclusion

- Using HALOE NO_x data indicates that the influence of the NO_x profiles is not very large but the discrepancy between measured and modeled DSCD's is showing the tendency of getting larger. Therefore the NO_x budget is unlikely to be responsible for this discrepancy.
- Changing parameters of the heterogeneous chemistry especially the hydrolysis of $BrONO_2$ increases the AM values for the BrO DSCD's but leaves the PM values almost unchanged. This effect reduces the difference between AM and PM DSCD values as observed in [3].

5 References

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Acknowledgements

We would like to thank the following for their support: AWI-Potsdam (measurements in Ny-Ålesund), MPI-Mainz (heterogeneous chemistry tool), FZ-Jülich (BRAPHO validation), Jörg Trentmann (BRAPHO) and Martyn Chipperfield (SLIMCAT).