VALIDATION OF GOME BRO AND OCLO OBSERVATIONS IN THE NORTHERN HEMISPHERE

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ABSTRACT

The Global Ozone Monitoring Experiment (GOME) measures solar back scatter spectra in a wavelength region from 240 to 790 nm from which atmospheric BrO and OClO columns could be derived using the well known DOAS method. In this study, GOME measurements are compared to column amounts derived from ground-based uv/vis measurements in Bremen (53°N, 9°E) and Ny-Ålesund (78°N, 12°E). The comparison has been made using only those GOME-pixels, having less than 200 km (Bremen) or 150 km (Ny-Ålesund) distance from the ground-based station.

In the case of BrO the comparison shows in general good agreement between the instruments. Especially tropospheric BrO-events in Ny-Ålesund could be clearly identified. An average vertical column of BrO of $5 \cdot 10^{13}$molec$\cdot$cm^{-2} could be estimated for both Bremen and Ny-Ålesund indicating only small latitudinal variations and higher values than expected from model calculations. In addition, only a small seasonal variation for the BrO vertical column at noon is evident. This is in contrast to recent experimental studies at twilight but well-known from models. The mean diurnal variation of OClO slant column amounts above Ny-Ålesund in March 1997 shows good agreement between GOME and ground-based measurements. Nevertheless the OClO evaluation from GOME shows often unreasonable values. The reason for this effect is still not clear.

1. INTRODUCTION

The instrument GOME (Global Ozone Monitoring Experiment (Ref. 4)) was launched onboard ERS-2 in April 1995. The GOME is a uv/vis double monochromator with a spectral range of 240–793 nm and a resolution of 0.2 nm (< 400 nm) and 0.4 nm (> 400 nm), respectively. GOME observes the light scattered from the earth's atmosphere and reflected on the ground in near nadir viewing geometry. Global coverage is achieved within 3 days at the equator and within 1 day at a latitude of 67°. The main goal of this instrument is to provide a high quality data set of total ozone and NO_2. As pointed out e.g. in (Ref. 8), advanced data products can evaluate from GOME spectra. Recently several authors have analysed measurements from GOME for BrO and OClO (e.g. (Refs. 10, 6, 19, 9, 23)).

BrO is known as an important trace gas in both troposphere (e.g. (Refs. 3, 14)) and stratosphere (e.g. (Ref. 15, and Refs. therein)). Therefore it is important to have a reliable global coverage data set of this trace gas. Further on validation with ground-based measurements might help in distinguishing tropospheric and stratospheric amounts of this trace gas. A detailed discussion of tropospheric BrO as seen by the GOME instrument can be found in (Ref. 18).

In the case of OClO it is well-known, that OClO is an qualitative indicator for chlorine activation. The reaction of ClO with BrO (Ref.16) is a rate limiting step in ozone depletion and couples chlorine and bromine chemistry. This reaction has three product channels, from which

$$ClO + BrO \longrightarrow Br + OClO \qquad (1)$$

is believed to be the major source for stratospheric OClO, relating the abundance of the OClO radical to those of BrO and ClO. Therefore GOME offers the unique opportunity to monitor the halogen activation in winter and spring in both hemispheres.

2. DATA ANALYSIS

GOME data and ground-based zenith sky measurements have been analysed for BrO and OClO using the DOAS technique. Calibrated earth shine and solar irradiance spectra from GOME were used as provided by ESA through DLR-DFD. From the GOME instrument all scans with solar zenith angle less than 93° have been included with the exception of the polar-viewing mode. The calculation of slant columns has been done using a direct sun spectrum taken from GOME in the same orbit. For the zenith-sky measurements the amount of the considered trace gas in the chosen reference has been estimated. The calculation of air mass factors (AMF) has been made by the means of the radiative transport model GOMETRAN++ developed at the iup Bremen (Ref. 20) to derive vertical columns.

2.1. Spectral fitting

For the BrO retrieval, a spectral fitting window of 344.7 - 359 nm was selected for all instruments. This spectral range was chosen to provide large differential BrO signals and small interference from other absorbers. In the fit, the absorption cross-sections of BrO (Ref. 24), O_4 (Ref. 12), NO_2 (Ref. 5) and O_3(Ref. 7) at 221 and 241 K have been used together with a synthetic Ring spectrum compensating the effect of Raman scattering in the atmosphere (Ref. 22). The wavelength calibration of BrO has been corrected by +0.17 nm as suggested by Aliwell et al. (Ref. 2) and recently confirmed by FTS measurements in Bremen (Ref. 11). After cross-calibration with the FTS measurements, both O_3 and NO_2 cross-sections have been shifted by +0.03 nm to correct for an error in wavelength calibration.

For OClO, a wavelength region of 365 - 390 nm has been chosen for the evaluation. The main advantage of this window is the negligible ozone absorption. Therefore only OClO (Ref. 25), O_4 and NO_2 together with the above mentioned Ring spectrum are necessary to derive OClO. Many tests have been made to minimise residuals. For this reason new FTS NO_2-cross sections have been used (Ref. 21).

The slit function of channel 2 of the GOME instrument is to narrow for sufficient sampling of the spectra with the diode array used as detector. Due to a small doppler shift, GOME earth-shine and direct sun measurements have a systematic difference of approximately 0.008 nm in the wavelength sampling. In addition, small thermal drifts of the instrument calibration have to be corrected in the fit. Therefore, interpolation of the earth-shine spectra is necessary for the analysis, leading to large residuals from undersampling errors. This can be accounted for by either averaging over adjacent spectral points and thus reducing the undersampling or by fitting a simulated undersampling spectrum as suggested by (Ref. 9). In this study, an undersampling spectrum and no smoothing were used. For evaluation of zenith-sky spectra a slight smoothing with a triangle function has been used.

2.2. Airmass factor

The DOAS fit results are slant columns, i.e., the integral of the absorber concentration along the line of sight. To convert slant into vertical columns, airmass factors (AMFs) for BrO have been computed with the radiative transfer model GOMETRAN++.

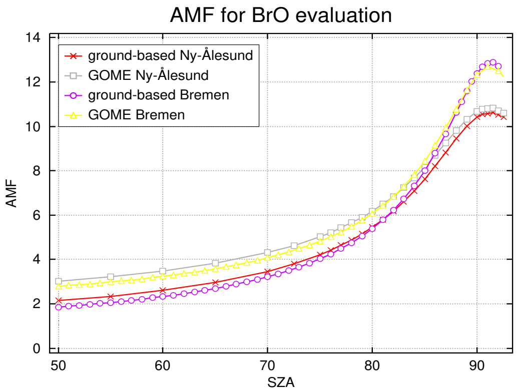

Figure 1. Airmass factors for BrO evaluation as provided by the radiative transfer model GOMETRAN++. All airmass factors are at 355 nm and include multiple scattering.

In figure 1 all AMFs used for the evaluation of BrO vertical columns are shown. Two profiles for BrO have been chosen taking into account the different latitudes. They were taken from two BrO measurements of (Ref. 13), one at high latitudes in February and one in mid-latitudes in November. However the differences in AMF for solar zenith angles below 80° are mainly due to differences in the albedo between Bremen and Ny-Ålesund.

2.3. Error discussion

Several error sources have to be considered for the accuracy of the DOAS retrieval: instrumental errors, systematic analysis errors and errors in the airmass factors.

The main systematic error source in the DOAS fit is the uncertainty in the BrO and OClO cross section, which is in the order of 20% for both. In addition, there are other, smaller error sources like stratospheric temperature changes, the I_0-effect or errors in the wavelength calibration that are discussed in detail in (Ref. 1). In the case of tropospheric BrO amounts uncertainties in airmass factors can exceed 50% and will dominate the total error of the vertical BrO columns (Ref. 18). In the case of a stratospheric profile this error can be estimated to be less than 20% as shown in figure 1.

3. RESULTS AND DISCUSSION

3.1. BrO

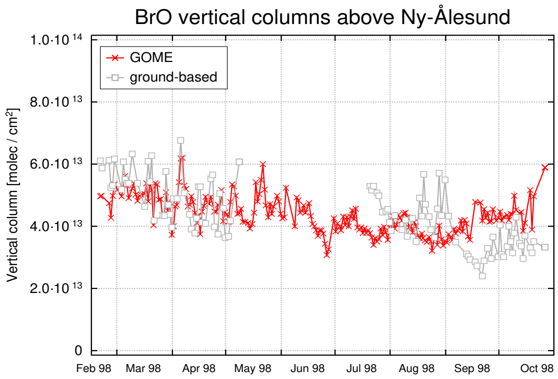

Figure 2. BrO vertical columns above Ny-Ålesund in 1998.

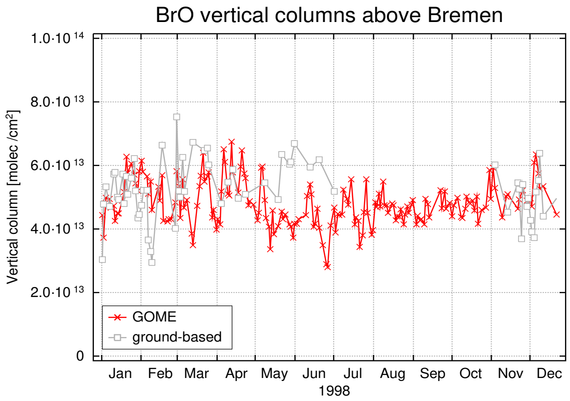

Figure 3: BrO vertical columns above Bremen in 1998.

In figures 2 and 3 the seasonal behaviour of the vertical column of BrO is shown for Ny-Ålesund and Bremen, respectively. The plotted values from GOME are daily mean values from all pixels within a šmallärea around the considered station. The calculated amounts of the ground-based station are synchronised to the mean GOME overpass. This method is used to minimise spatial and temporal differences in the considered BrO column. For the reason, that the BrO profile used for the radiative transport calculations is only stratospheric, high tropospheric BrO columns during low ozone events are underestimated (for example in the beginning of April in Ny-Ålesund). Gaps in the zenith sky time series are due to instrumental problems (Bremen) and to small differences in the solar zenith angle with respect to the chosen Fraunhofer reference spectrum (Ny-Ålesund).

From both figures it is obvious, that the agreement in the total column is good with the exception of the fall 1998 in Ny-Ålesund. The vertical column decreases from winter towards summer from $5.5 \cdot 10^{13}$molec$\cdot$ cm^{-2} to approximately $4 \cdot 10^{13}$molec$\cdot$ cm^{-2}. The reason for the behaviour in fall 1998 is yet unknown but possibly due to instrumental drifts in the ground-based measurements. Detailed structures in the time series correspond only poorly with the exception of tropospheric BrO events. One possible reasons is the low signal/noise ratio for small solar zenith angles particular in the case of zenith sky measurements. Another reason is the use of inappropriate air mass factors (for example changes of the tropopause height, in the albedo or in the tropospheric column, have a large influence on the AMF).

The mean vertical column derived from this study ($5 \cdot 10^{13}$molec$\cdot$ cm^{-2}) is about 50% higher than the values, obtained from model runs (Ref. 17) and integrated balloon profiles (Ref. 13) provide.

3.2. OClO

As pointed out before, GOME provides global coverage of the amounts of OClO and thereby an overview, where chlorine activation taking place. Therefore near real-time evaluation might help to plan activities within the scope of campaigns like HIMSPEC in THESEO. In cooperation with the IUP Heidelberg the IUP Bremen are currently producing plots like figure 4 to satisfy this requirements.

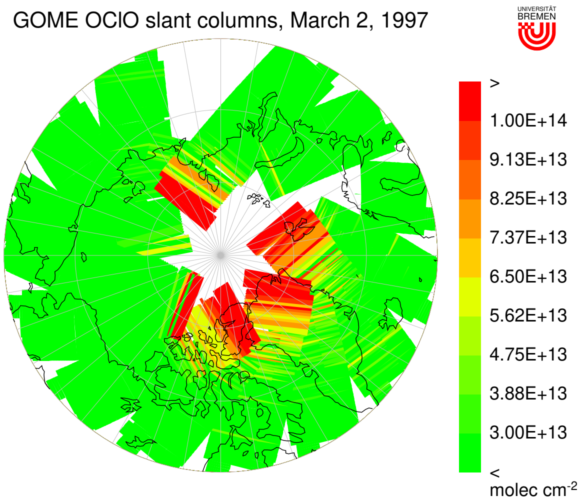

Figure 4. OClO slant column amounts in the northern hemisphere on March 2, 1997.

Figure 5 includes all OClO slant columns, derived from spectra in March 1997, when Ny-Ålesund was well located inside the polar vortex. As for BrO, only GOME pixels within a 150 km radius around the station were considered. The derived amounts from zenith-sky are mean values interpolated on a set of solar zenith angles. The agreement between both data sets is quite good. Higher values from GOME for small solar zenith angles are expected because of higher air mass factors for this case. However, some problems in evaluating OClO from GOME data remain. For example it is still unknown, why the chosen Fraunhofer reference has a large influence on the results. This is true only in the northern hemisphere! In addition the absorption cross section from the most important absorber in the used fitting window O_4 is poor in both differential values and in the wavelength calibration.

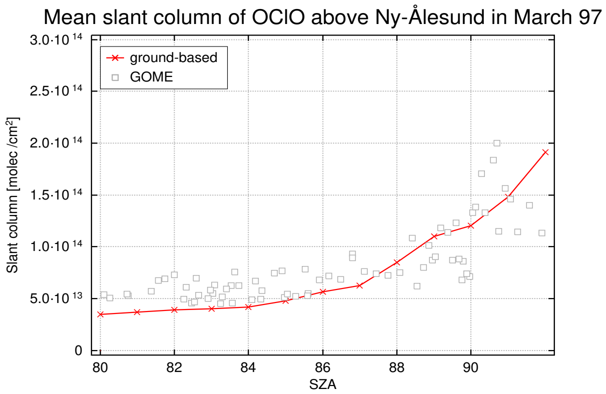

Figure 5. OClO slant columns evaluated from both, GOME and ground-based instrument for March 1997.

4. SUMMARY

This study shows the large benefit from GOME providing reasonable data sets for OClO and BrO for the scientific community. While the GOME BrO evaluation has converged to a high quality, the OClO evaluation still contains a lot of open questions.

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