Seasonal and diurnal variations of BrO column abundances above Harestua (60° N) and Haute-Provence (44°N) during THESEO

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Abstract
BrO measurements from ground-based zenith-sky UV-visible spectrometers operated in the frame of the European Stratospheric BrO project at Harestua (60°N) and Observatoire de Haute Provence (OHP, 44°N) are reported over the period from January 1998 until July 1999. Measured BrO differential slant columns show clear latitudinal differences, most observed features being well captured by model simulations from the SLIMCAT 3D chemical transport model. BrO vertical columns derived from zenith-sky observations and from the Global Ozone Monitoring Experiment (GOME) show large values around noon, which can only be understood by assuming the presence of significant amounts of BrO in the troposphere. Results further indicate that the proposed tropospheric BrO would have a strong diurnal cycle with a maximum around noon.

1. Introduction

Halogen oxides are playing a key role in the catalytic processes that control the O_3 abundance in the lower stratosphere. Despite being far less abundant than chlorine in the stratosphere, bromine is playing a significant role because of its very high efficiency in destroying ozone, and because of its interaction with the ClO_x, NO_x and HO_x cycles. BrO, the most abundant bromine species during sunlit can be measured by UV-visible spectroscopy from ground-based, balloon and satellite platforms.

Our aim is to provide high quality long-term continuous observations of BrO total columns from two ground-based stations (Harestua, 60°N, and OHP, 44N°) sampling different latitudinal regions. Main objectives are (1) to contribute to a better characterisation of the BrO diurnal, seasonal, latitudinal and interannual variations, (2) to test model simulations against measurements, and (3) to contribute to a better assessment of the overall consistency of multi-platforms BrO observations.

2. Measurements

The measurements reported in this work have been performed using UV-visible spectrometers designed and assembled at IASB-BIRA for zenith-sky observations in the framework of the Network for the Detection of Stratospheric Change (NDSC). Optimal sensitivity is obtained through use of cooled array detectors, thermal regulation of spectrometers and proper elimination of polarisation artefacts [1]. BrO slant column abundances are retrieved by differential absorption spectroscopy (DOAS) in the wavelength interval 346-359 nm, following recommendations issued in Aliwell *et al.* [2].

3. Results

(i) Observed and modeled twilight BrO slant columns

Fig. 1, left panel, shows time-series of BrO differential slant columns densities (DSCDs) measured at the two stations, for solar zenith angles 90° - 80°. These observations are roughly consistent with other BrO measurements performed at similar latitudes [3-4]. Main advantages of twilight observations are (1) best sensitivity to the stratosphere, and (2) possibility to gain information on bromine chemistry through investigation of the BrO conversion into its nighttime reservoirs.

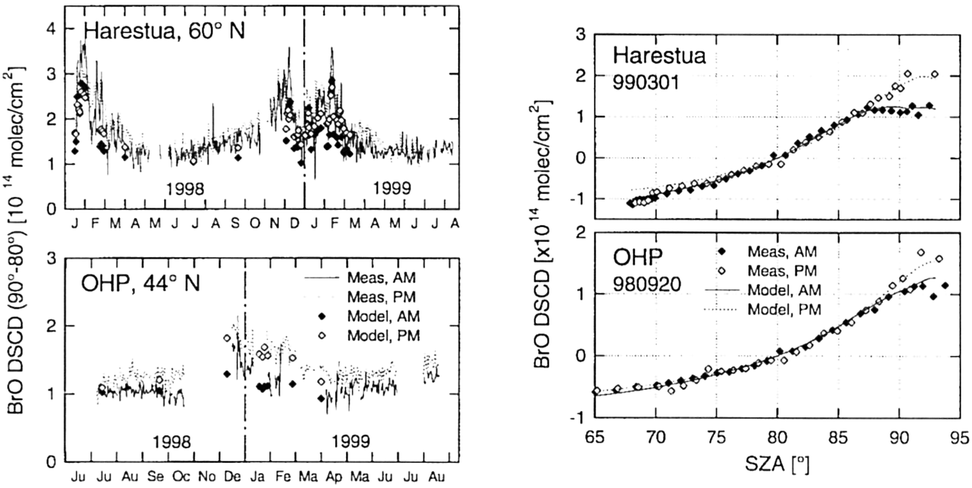

Figure 1. Comparison between observed and modeled BrO DSCDs for Harestua and OHP stations. Time-series (left panel) range from January 1998 to August 1999. On the right panel, the solar zenith angle evolution of the modeled and measured DSCDs is shown for two selected dates.

Measured BrO DSCDs have been compared with preliminary model simulations, shown together with observations in Fig. 1. The slant column model used in this study is based on a 1D photochemical box-model coupled to a single-scattering ray-tracing software suite developed at IASB-BIRA. Initialisation was provided by the 3D chemical transport model SLIMCAT [4]. The model and its validation are described by Hendrick *et al.* [5]. First model calculations reported here appear to capture most observed features, e .g. events of high BrO DSCDs in winter at Harestua (related to advection of chlorine activated polar vortex air) or large winter-time AM/PM variation at OHP. Solar zenith angle dependences shown in Fig. 1, right panel, for two selected days, further confirms the ability of the model to reproduce BrO variations over a large range of solar zenith angles.

(ii) BrO vertical columns from Langley plot analysis

Although straightforward in principle, the conversion from slant to vertical columns is complicated by the lack of knowledge on the vertical distribution of BrO, particularly in the lowest part of the atmosphere, and by the diurnal variation of the molecule. Assuming constant BrO around noon, vertical column densities (VCDs) can be derived from the slope of a Langley plot calculated for a selected range of solar zenith angles. This approach has been used in Fig. 2 where zenith-sky BrO VCDs retrieved in three different solar zenith angle ranges are compared to coincident GOME BrO columns.

Results clearly show a significant increase of the zenith-sky BrO columns at high sun together with an improvement of the agreement with GOME as the time of analysis approaches noon, i.e. also the time of the GOME overpass. Good matching with GOME however can only be obtained with Harestua data, at least in the range of solar zenith angles sampled here.

Excluding possible instrumental artefacts, the observed behaviour suggests a large diurnal variation of BrO due to photochemical reactions. However the large noon values are not consistent with current stratospheric bromine chemistry and budget, which therefore points to the presence of a significant contribution from BrO present in the troposphere, as also discussed by Richter *et al.* [3] and Pundt *et al.* [6]. The small solar zenith angle dependence of the zenith-sky BrO VCDs at OHP suggests that the proposed tropospheric BrO amounts would show a marked diurnal variation, with a maximum around noon and a strong decrease occuring either before twilight (OHP) or possibly during twilight (Harestua). Possible explanations for this behaviour remain to be explored.

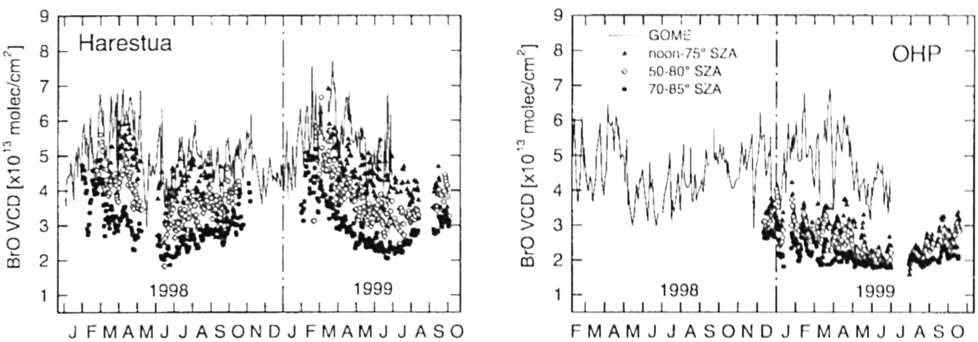

Figure 2. BrO vertical columns derived from Langley plot analysis of ground-based data at Harestua and OHP (symbols), in comparison to BrO columns evaluated from analysis of GOME data. The solar zenith angle variation of the BrO zenith-sky vertical column is displayed.

(iii) Noon BrO vertical columns

Langley plot analysis are limited towards noon, especially at mid-latitude, because air mass factors tend to become small and independent of the solar zenith angle at high sun. At the same time, the error bars of the zenith-sky data increases. In order to try and obtain better estimation of noon BrO VCDs needed for comparison with GOME, an alternative method has been applied where zenith-sky data are analysed exactly at noon time using a single, fixed, reference spectrum. Main difficulties of this appoach are the necessity to estimate the residual BrO amount (R) in the reference spectrum, and the need for good instrumental stability over long periods of time. Noon BrO VCDs retrieved in this way at Harestua and OHP are shown in Fig. 3.

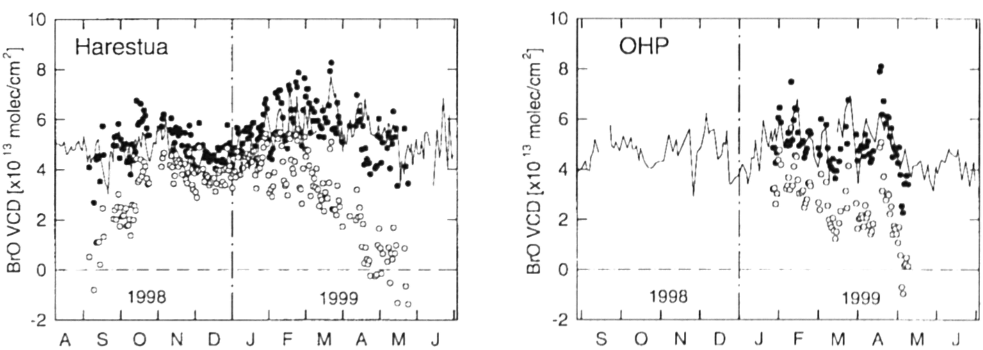

Figure 3. Zenith-sky BrO vertical columns derived at noon using a single reference spectrum (black dots), compared to GOME BrO values (solid line). The figure also shows the sensitivity of the zenith-sky data evaluation to the determination of the BrO residual amount in the reference spectrum (see text).

For these evaluations, reference spectra were selected on March 25 at both sites. Compared to Langley plot VCDs shown in Fig. 2, it is obvious that the noon evaluation using a fixed reference spectrum greatly improves the agreement between ground-based and GOME BrO data, especially at OHP. Note in particular the good agreement for short-term variations, not dependent on the estimation of the residual amount in the reference spectrum. To further test the sensitivity of the method to this critical parameter, an additional evaluation has been performed where the value of R was reduced by a factor of two. Results of this test are represented by open circles in Fig. 3. Unrealistically low BrO values are obtained at high sun in spring when the sensitivity to R is largest, which adds to our confidence in the initial evaluation.

5. Conclusion

Zenith-sky UV-visible BrO measurements have been performed at Harestua (60°N) and OHP (44°N) over the period from January 1998 until August 1999. BrO differential slant columns have been compared with preliminary model simulations using the IASB-BIRA slant column model, initialised by the SLIMCAT 3D chemical transport model. The good agreement obtained suggests that the stratospheric bromine chemistry is currently well understood, as further demonstrated in a parallel study by Sinnhuber *et al.* [4].

BrO vertical columns derived from zenith-sky data using two different approaches have been compared to GOME BrO evaluations. Good agreement can only be obtained if zenith-sky data are evaluated at the time of the GOME overpass. In the current state of the data interpretation, results suggest large amounts of tropospheric BrO being present at both sites around noon. The same results further suggest that this tropospheric BrO would display a marked diurnal variation, possibly not in phase with BrO in the stratosphere.

Acknowledgements

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