GOME measurements of stratospheric and tropospheric BrO

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ABSTRACT

Measurements from the Global Ozone Monitoring Experiment (GOME) have been analysed for BrO absorptions using the Differential Optical Absorption (DOAS) method. By introducing a correction for a small angle dependency of the diffusor used for the direct sun measurements in the GOME instrument, the overall consistency of the BrO data set could be improved significantly. Evidence is found for large tropospheric contributions to the BrO columns measured by GOME, both from BrO in the polar boundary layer in spring and a global BrO background, probably located in the free troposphere and present throughout the year. The latter has been further investigated by comparing BrO and O_4 columns above the remote Pacific, resulting in an estimate of 0.5 – 2ppt of uniformly mixed BrO in the troposphere, in agreement with previous studies.

INTRODUCTION

The Global Ozone Monitoring Experiment (GOME) is a UV/visible spectrometer on board of the European satellite ERS-2. GOME is a 4 channel double monochromator covering the wavelength range of 230 – 800 nm with a spectral resolution of 0.2 – 0.4 nm. ERS-2 was launched into a polar sun-synchronous orbit in April 1995. With a ground pixel size of 40×320 km^2 (40×960 km^2 for the back scan) GOME reaches global coverage at the equator within 3 days. The main objective of GOME is the global measurement of ozone columns, but other trace gases such as NO_2, SO_2, HCHO, BrO and OClO can be retrieved from the spectra as well (*Burrows et al.* [1999]).

Bromine Oxide measurements with GOME have been the focus of several papers, dealing with the analysis method (*Hegels et al.* [1998]; *Chance* [1998]) and enhanced BrO in the polar boundary layer in spring (*Wagner and Platt* [1998]; *Richter et al.* [1998]). In this study, BrO columns for 1999 and 2000 have been derived from GOME spectra using an improved data analysis scheme. The results are discussed in view of the implications for BrO in the boundary layer, the free troposphere and the stratosphere.

DATA ANALYSIS

GOME lv1-spectra have been analysed using the IUP Bremen Differential Optical Absorption (DOAS) algorithm to derive slant columns of BrO in the 345 – 359 nm wavelength region. The settings for the fit are similar to those used for ground-based zenith-sky BrO measurements. Vertical columns have been computed with the radiative transfer model GOMETRAN (*Rozanov et al.* [1997]) using a simple stratospheric profile, resulting in a significant underestimation of tropospheric contributions. Details on the analysis method can be found elsewhere (*Richter et al.* [1998, 1999]). Here, we report an additional step in the data evaluation that leads to much more consistent BrO columns from GOME measurements.

One important difference between ground-based zenith-sky and GOME measurements is the use of an extraterrestrial solar spectrum as a background. In principle, this enables GOME to measure absolute slant columns, in contrast to ground-based measurements that have to account for the unknown absorber column in the background spectrum. With GOME, the earthshine spectra are recorded using a scan mirror whereas the solar spectrum is measured via a reflecting diffuser plate to reduce the intensity. Unfortunately, small variations in the incident angle of the light on the diffuser plate lead to changes in the spectrum of the reflected light. This has been revealed during the calibration of the SCIAMACHY instrument, that employs a similar diffuser. During one year, the position of the sun relative to the GOME diffuser varies slightly. This small change introduces systematic changes in spectral structures,

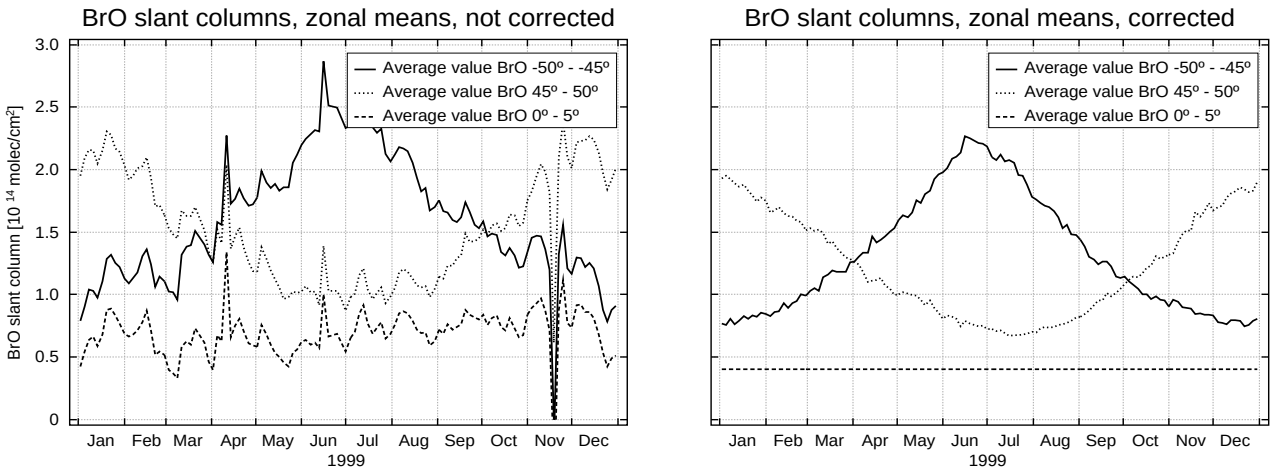

Fig. 1. Effect of the correction of the angle dependence of the GOME diffuser plate on the BrO slant columns. In the correction, it is assumed, that BrO over the equator is constant with a column of $4 \cdot 10^{13}$ molec/cm^2.

that can interfere with the retrieval of weak absorbers. A similar problem has previously been identified in the NO_2 retrieval (*Richter and Burrows* [2000]) where it was solved by using one single solar background spectrum for all data. However, in channel 2 of the GOME instrument, temporal changes of the detector etalon can not be neglected. Therefore, using a single background spectrum is not feasible over periods longer than a few days for the BrO analysis.

As an alternative approach, one can assume that BrO columns over the equator are small and do not show a significant seasonal variation. This assumption is justified by the fact, that in low latitudes BrO is mainly released by photolysis of HOBr and $BrONO_2$, and that the actinic flux in the stratosphere at noon does not vary significantly near the equator. If BrO is constant over the equator, then all variations in GOME BrO measurements over that region are an instrumental artefact and should be corrected. Consequently, for every GOME orbit the BrO slant columns over the equatorial region ($\pm 5°$) are averaged and the difference to the assumed constant value is subtracted from all BrO columns of the orbit. This procedure results in much smoother seasonal variations of GOME BrO slant columns as illustrated in Figure 1.

It has to be noted, that the choice of the constant column at the equator represents one more free parameter in the analysis that can not be determined from the GOME data themselves. However, not applying the correction is equivalent to using an unknown and varying offset. As the offset has to be applied on the slant columns, it is much more important at low latitudes than at high latitudes and during winter/spring. The current choice of $4 \cdot 10^{13}$ molec/cm^2 roughly corresponds to the BrO columns predicted by the SLIMCAT model (*B.M. Sinnhuber, private communication*), consistent with the assumption that little tropospheric BrO is present at equatorial regions. As discussed below, a larger value might be appropriate but this result needs to be confirmed prior to implementation.

GLOBAL BEHAVIOUR OF BrO

Using the improved analysis scheme, zonal averages of BrO have been computed for all GOME measurements taken in 1999 as shown in Figure 2 for both hemispheres. As can be seen from the figures, the seasonal variation of BrO in both hemispheres is smooth and reproducible at all latitudes. This is highlighted at the December to January transition in the Southern Hemisphere plot, where no jump occurs although the measurements are one year apart. At low and mid-latitudes in both hemispheres, BrO columns are smallest in summer and larger in winter. The exact magnitude of this variation depends on the assumed value of the BrO column over the equator, but no reasonable choice of this offset will lead to a curve without summer minimum. In both hemispheres, BrO columns increase with latitude in all seasons with exception of the measurements at large solar zenith angle (high latitudes in winter) where stratospheric BrO is expected to be lower as a result of reduced photolysis from the reservoirs. Differences between the two hemispheres exist with respect to the spring BrO maximum, that is related to BrO in the boundary layer (see next section): In the North, spring values are larger at high and mid-latitudes, whereas in the South the spring increase

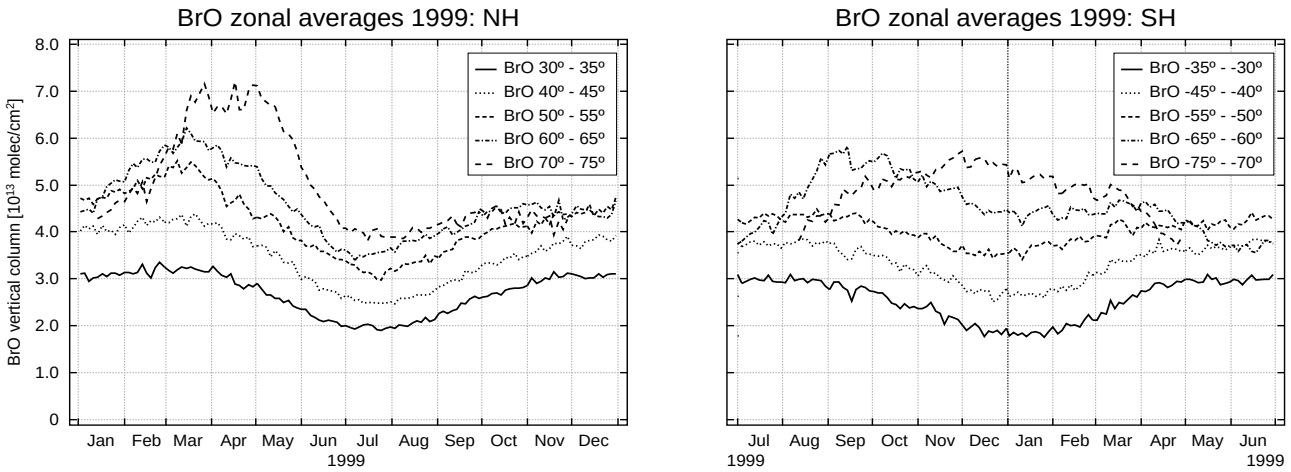

Fig. 2. Zonal averages of BrO vertical columns in both hemispheres 1999. The Southern Hemisphere has been offset by 6 months for better comparison. Note that the December - January transition in the Southern Hemisphere is smooth although the measurements are one year apart.

is restricted to the 60°– 65° latitude band. In addition, a summer maximum is observed at even higher latitudes above Antarctica.

Some of the general features of the BrO global distribution are in qualitative agreement with model predictions for stratospheric BrO. A latitudinal variation is expected as a result of the change in tropopause height from the tropics to the poles (*Wagner* [1999]). As most of the stratospheric BrO is located in the lowermost stratosphere, changes in tropopause height have a strong influence on the vertical column and can explain BrO variations of up to a factor of two. A winter maximum at high latitudes is also expected as subsidence in the polar vortex will lead to some increase in BrO. However, the high absolute value of the observed vertical columns as well as the strong seasonal variation are not predicted by models. In particular, the high spring values in the Northern Hemisphere and the summer maximum in the Southern Hemisphere can not be explained by stratospheric BrO even if all Br_y is converted to BrO. It is therefore concluded, that significant amounts of BrO must be present in the troposphere, and that two separate effects play a role, one more episodic at high latitudes in spring and one that leads to a slowly varying offset at all latitudes.

BrO IN THE BOUNDARY LAYER

Very large BrO columns are observed in each polar spring in both hemispheres. These events have already been studied in previous papers (*Wagner and Platt* [1998]; *Richter et al.* [1998, 1999]) and are attributed to boundary layer BrO. This interpretation is supported by coincident measurements from the ground and the correlation with low ozone events and changes in the ratio of gaseous to particulate mercury compounds.

In Figures 3 and 4, monthly averages are shown for the winter/spring season 1999 (Southern Hemisphere) and 1999/2000 (Northern Hemisphere). As in previous years, strongly enhanced BrO columns are observed in spring over sea ice and along the coast lines of the Arctic Ocean and Antarctica. The difference in sea ice distribution between the two hemispheres is reflected in the different BrO distribution, that is centred over the pole in the Northern Hemisphere but has a more ring like structure in the South. These differences explain also part of the hemispheric asymmetry discussed in the previous section, where zonal averages peaked at higher latitudes in the North than in the South. The December data over Antarctica illustrate the formation of a stable BrO maximum over the continent, that has no equivalent in the North and has already been pointed out in the discussion of Figure 2. Two possibilities exist for the sources of summer BrO over Antarctica. Either, it is related to the boundary layer BrO formed over sea ice earlier in the year, for example by transport of a bromine containing precursor from the coast to the continent, or it is formed locally. In the latter case, a new mechanism for the BrO formation is needed, that is active at high sun and does not rely on pre-processing on sea ice. This issue remains open and will have to be investigated further.

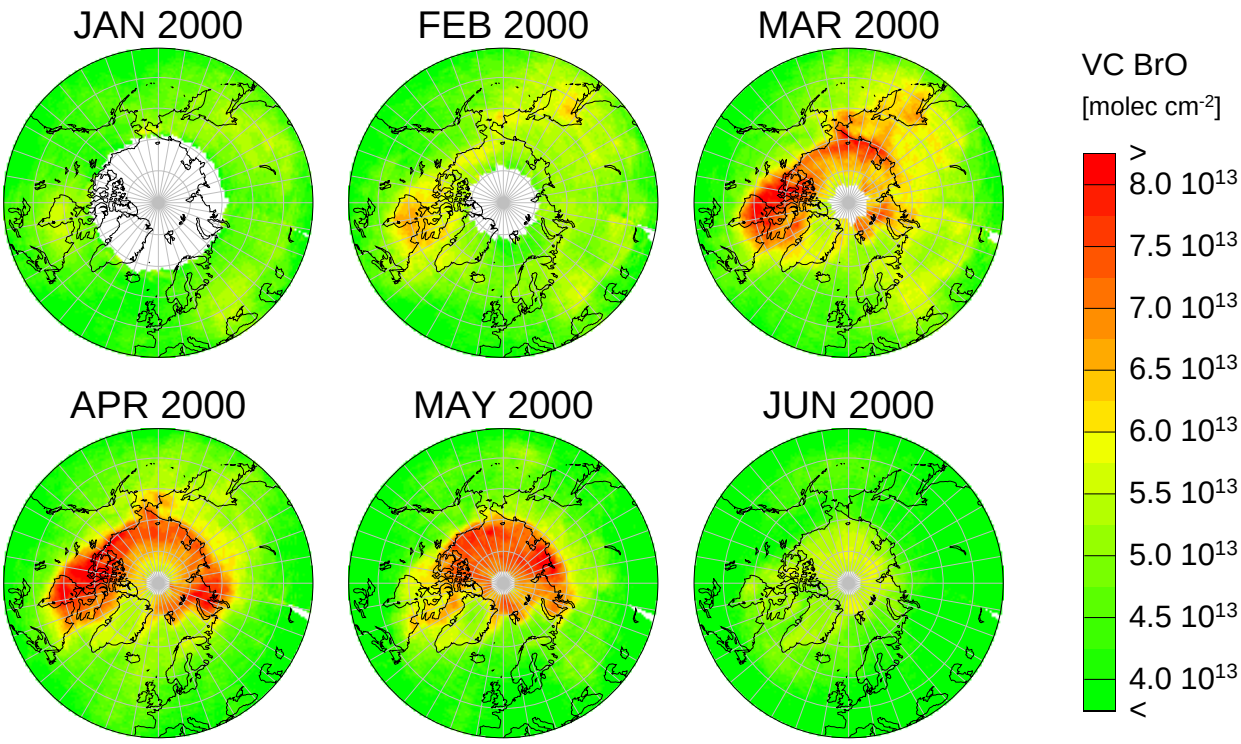

Fig. 3. Monthly averages of BrO vertical columns in winter/spring 2000 for the Northern Hemisphere. The high values above the polar region and the Hudson Bay area result from enhanced BrO concentrations in the boundary layer. The airmass factor used is based on a stratospheric BrO profile leading to an underestimation of the boundary layer BrO.

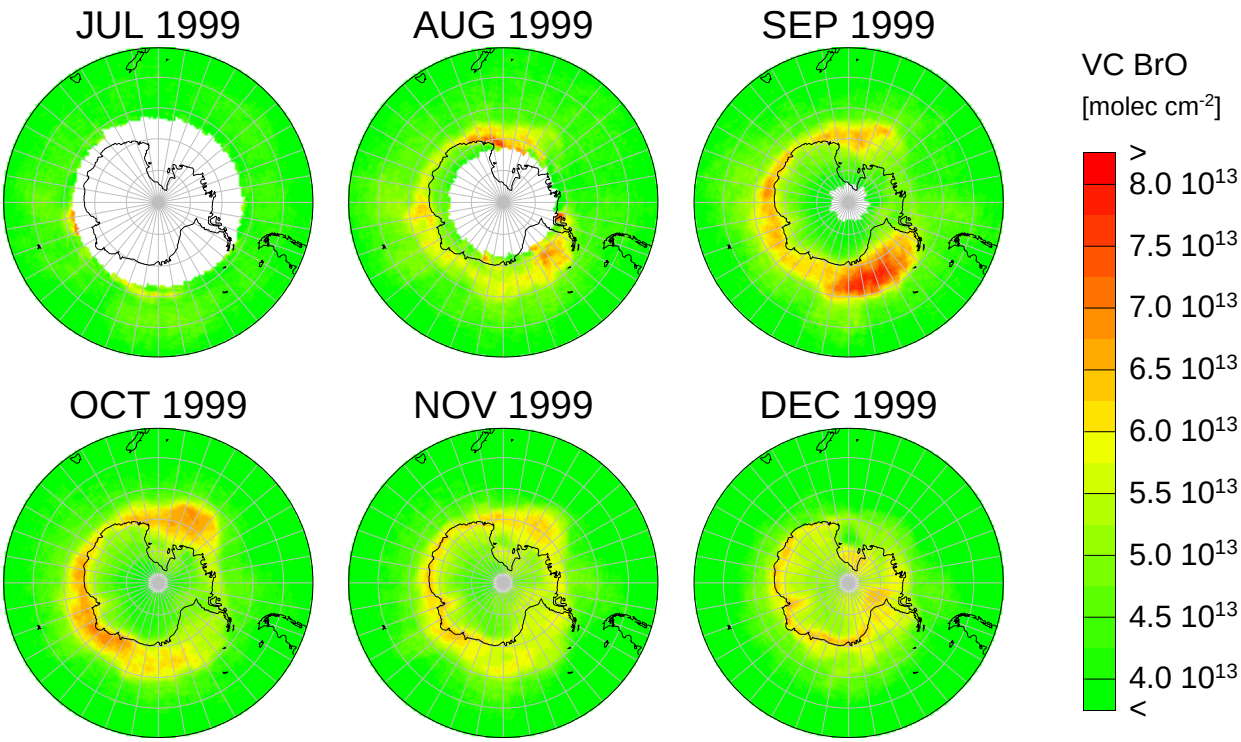

Fig. 4. Same as Figure 3, but for the Southern Hemisphere. The difference in data coverage in autumn is a result of the difference in local time for the GOME overpass in the two hemispheres.

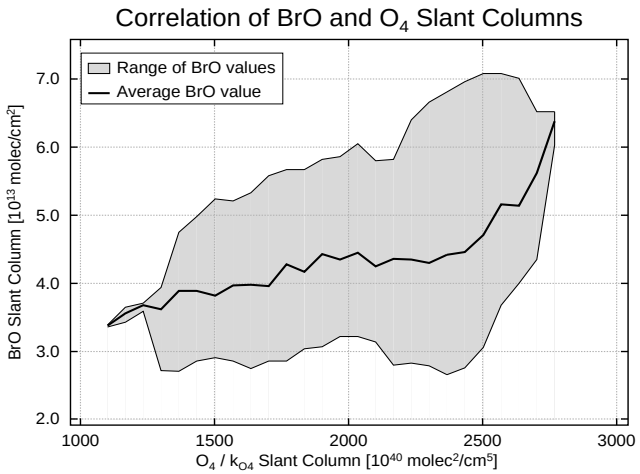

Fig. 5. GOME BrO slant columns over the Pacific (170°E, 10°S- 260°E, 10°N) in February 1999 as a function of simultaneously determined O_4 column. While the scatter of data is large, a general correlation between large BrO and large O_4 values indicates that a significant amount of BrO is located in the troposphere over the remote Pacific.

BrO IN THE FREE TROPOSPHERE

Comparison of GOME BrO vertical columns with models, balloon-borne observations and ground-based measurements in previous studies (*Pundt et al.* [2000]; *Fitzenberger et al.* [2000]; *Wagner* [1999]; *Wagner et al.* [2000]; *VanRoozendael et al.* [1999]) has lead to the conclusion, that a significant tropospheric background of several ppt BrO must be present in the atmosphere at all latitudes. This assumption has been tested by correlating GOME BrO columns taken in February 1999 over the remote equatorial Pacific (170°E, 10°S- 260°E, 10°N) to the simultaneously measured O_4 columns as derived in the 350 – 380 nm region. O_4, the dimer of atmospheric oxygen can be used as a qualitative indicator of the tropospheric light path as the vertical profile is constant and strongly weighted towards the lower troposphere. It is however important to use O_4 absorption structures at wavelengths close to the BrO fitting window to ensure that the radiative transfer is similar for both absorbers.

Variations in tropospheric light path arise mainly from changes in cloud cover and cloud top height and - to a lesser degree - changes in aerosol loading and surface albedo. No simple relation exists between O_4, cloud cover and cloud top height, but in first approximation low O_4 columns correspond to situations with high clouds and high O_4 columns to cloud free scenes. As an exception, the largest O_4 columns are expected for situations with very low clouds, but for a qualitative discussion this does not pose a problem as tropospheric BrO columns should also be larger under these conditions.

In Figure 5, the resulting scatter plot and the mean value is shown for February 1999 over the Pacific region. This location has been selected, as it should represent an unpolluted background situation, should not be influenced by polar spring boundary layer BrO events and stratospheric BrO is expected to be stable in both time and space. Also, near the equator the variation in solar zenith angle in the GOME measurements is small, facilitating the use of slant columns in the comparison. As can be seen from the plot, a general correlation exists between low BrO and low O_4 columns. Similarly, the largest BrO columns are seen in cloud free pixels. This result suggests, that a considerable amount of BrO is present in the troposphere below cloud top height. The fact, that the low BrO values are seen for all cloud situations points at some variability in the tropospheric BrO concentrations. From the data, the tropospheric BrO contribution to the measured slant column can be estimated to be up to $4 \cdot 10^{13}$ molec/cm^2, corresponding to 0.5 – 2 ppt of uniformly mixed BrO in the troposphere. This is in good agreement with previous estimates.

Some care must be taken when interpreting the results, as the scatter in the BrO columns is large at the small solar zenith angles over the equator, and other parameters such as intensity and Ring filling-in also change with cloud cover. In addition, the need for correcting BrO columns with an assumed constant value over the equator introduces some uncertainty about the absolute values. For this analysis, the average over all equatorial GOME BrO measurements of one day has been used to correct for the changes in day to day values without interfering with the modulation by

clouds. Clearly, more detailed studies are necessary to confirm the results and come to quantitative results.

SUMMARY

GOME measurements have been analysed for BrO using the DOAS method. It has been shown, that a significant improvement in overall data consistency can be achieved by using the equatorial measurements to correct for the day to day variations introduced by the diffusor plate used for direct sun measurements from GOME. The seasonal variation of BrO columns in both hemispheres is similar with a maximum in winter and an increase with latitude. This is in qualitative agreement with model predictions for the stratospheric BrO. However, the vertical BrO columns measured by GOME are much larger than what can be explained by the stratospheric Br_y, indicating significant contributions of tropospheric BrO. In polar regions, large areas of enhanced boundary layer BrO associated to low ozone events are observed in both hemispheres in spring. Boundary layer BrO is mostly located over sea ice and along the coast lines and shows somewhat higher values in the Northern Hemisphere. A persistent summer maximum of BrO over the Antarctic continent hints at large tropospheric BrO concentrations in that regions, but it is yet unknown in what height this BrO resides and what the release mechanisms could be. Comparison of BrO and O_4 columns over the equatorial Pacific shows a clear correlation between the two quantities, indicating the presence of 0.5 – 2 ppt of BrO in this remote part of the troposphere, in agreement with results from other studies.

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