INTERCOMPARISON OF BrO MEASUREMENTS FROM ERS-2 GOME, GROUND-BASED AND BALLOON PLATFORMS

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ABSTRACT

The consistency of BrO column amounts derived from GOME spectra and from correlative ground-based and balloon measurements performed in 1998-1999 during the Third European Stratospheric Experiment on Ozone (THESEO) has been investigated. The study relies on UV-visible observations at several mid- and high latitude ground-based stations in both hemispheres, complemented by balloon-borne solar occultation profile measurements and 3D chemical transport model simulations. Previous investigations have reported GOME BrO columns systematically larger than those deduced from balloon, suggesting BrO being present, possibly ubiquitously, in the free troposphere. The robustness of this hypothesis has been further tested based on the presently available correlative data set. It is shown that when accounting for the BrO diurnal variation and the solar zenith angle dependency of the sensitivity of correlative data to the troposphere, measurements from all platforms are consistent with the presence of a tropospheric BrO background of 1-3 $x10^{13}$ molec/cm^2 extending over mid- and high latitudes.

INTRODUCTION

Launched in April 1995 on the ESA ERS-2 platform, the Global Ozone Monitoring Experiment (GOME) is a 4-channel spectrometer covering the region from 230 to 800 nm with a spectral resolution of 0.2 – 0.4 nm (Burrows et al, 1999a). Although the main objective of GOME is the global measurement of ozone columns, other trace gases can also be retrieved from the spectra like NO_2, OClO, SO_2, H_2CO and BrO. The potential of GOME to monitor the important ozone destroying catalyst BrO in both the troposphere and the stratosphere has been highlighted in a number of publications (e.g. Hegels et al., 1998; Wagner and Platt, 1998; Richter et al., 1998). In most of these studies GOME has been used to characterise the spectacular development of highly concentrated BrO plumes produced in the polar planetary boundary layer of both hemispheres in spring (the so-called bromine explosion phenomenon). Further analysis of GOME BrO observations also suggested the existence of a large-scale background of free-trospospheric BrO, with fundamental implications for the tropospheric chemistry (Platt, 1997).

The fine interpretation of the GOME BrO observations, in particular those related to the free-tropospheric BrO issue, requires a careful assessment of the accuracy of the measurements under a variety of conditions (latitudes, seasons, solar zenith angle, etc). In the absence of any other BrO product available from space, this can only be achieved through validation exercises involving BrO correlative measurements from the ground, balloon or aircraft. The purpose of this study is precisely to test the consistency between spectroscopic observations of BrO from GOME and from a large set of ground-based and balloon observations obtained within the European THESEO Stratospheric BrO project (1998-2000).

GOME BrO DATA ANALYSIS

Owing to the similarity between GOME and the UV-visible spectrometers operated on the ground and from balloons, the analysis for BrO from GOME can be made using tools and concepts originally developed for other

platforms (Hegels et al., 1998; Richter et al., 1998; Wagner and Platt, 1998). Although simple in principle, the retrieval of atmospheric BrO by the method of differential optical absorption spectroscopy (DOAS) is complicated by the fact that the absorptions to be measured are extremely small (typically of the order of 0.1% or less). Achieving good accuracy therefore requires great care in controlling many aspects of the analysis and spectral data characterisation. Key parameters in BrO data processing, including in particular the use of accurate and precisely calibrated laboratory reference data sets measured at stratospheric temperatures (Burrows et al., 1999b), as well as the design of appropriate corrections for the Ring effect (Chance and Spurr, 1997; Vountas et al., 1998) and for the GOME undersampling (Chance, 1998), have been progressively identified resulting in significant improvements of the data consistency not only from GOME but also from balloon and ground-based instruments (Aliwell et al., 2001). Currently the uncertainty on the GOME BrO slant column evaluation is thought to be limited by the 5-7% uncertainty in the absorption cross-section (Wilmouth et al., 1999) and by the absolute uncertainty of $\pm 3.10^{13}$ molec/cm^2 due to the GOME diffuser plate artefact recently identified by Richter et al. (2001).

CORRELATIVE DATA SETS

Correlative measurements used in this work are for the most part those associated with the THESEO-Stratospheric BrO project (Van Roozendael et al., 2000). These include observations from a network of ten UV-visible zenith-sky spectrometers covering mid- and high latitudes of both hemispheres (Sinnhuber et al., 2001 and references therein). Ground-based measurements are complemented by a series of about twenty BrO profiles obtained in various latitudes and seasons using two balloon-borne solar occultation instruments, the SAOZ-BrO (Système d'Analyse par Observation Zénithales optimised for BrO, Pundt et al, 1996) and the LPMA/DOAS (Laboratoire de Physique Moléculaire et Applications / Differential Optical Absorption Spectroscopy, Fitzenberger et al, 2000).

Measurements from the ground, from balloon and from space are characterised by different sensitivities to the BrO vertical distribution. The balloon-borne solar occultation technique is best suited for stratospheric observations above the tropopause region, however, as shown below, the technique can be extended to lower altitudes under favourable circumstances. Ground-based observations are usually made at twilight when they show optimal precision and large sensitivity to the stratosphere. In contrast GOME, measuring the nadir radiance at noon (10h30 local time), is very sensitive to the troposphere for most parts of the orbit. These characteristics have to be considered when comparing GOME BrO to other data sets. In addition, it has to be kept in mind that BrO is a photochemically active species displaying a pronounced diurnal variation. Therefore differences in the timing of the observations are likely to affect the comparisons and must be taken into account.

RESULTS AND DISCUSSION

Initial attempts to validate GOME BrO observations were made using integrated BrO profiles obtained from stratospheric balloon measurements. A good illustration of the typical behaviour observed in these comparisons is given in Figure 1, which is an update of the work described in Pundt et al. (2000). In this Figure, GOME BrO columns computed in a radius of 500 km around correlative launch sites are compared to a number of integrated BrO profiles measured at various latitudes and seasons by the SAOZ-BrO instrument, and to calculated stratospheric BrO columns from the 3D chemical transport model SLIMCAT (Chipperfield, 1999). One can see that GOME BrO columns are systematically larger than both balloon and 3D-CTM results. The difference of 1-3 $x10^{13}$ molec/cm^2 is larger than known uncertainties on both measurement sources. Model values extracted at noon instead of twilight also indicate that this difference cannot be explained by the diurnal variation of stratospheric BrO.

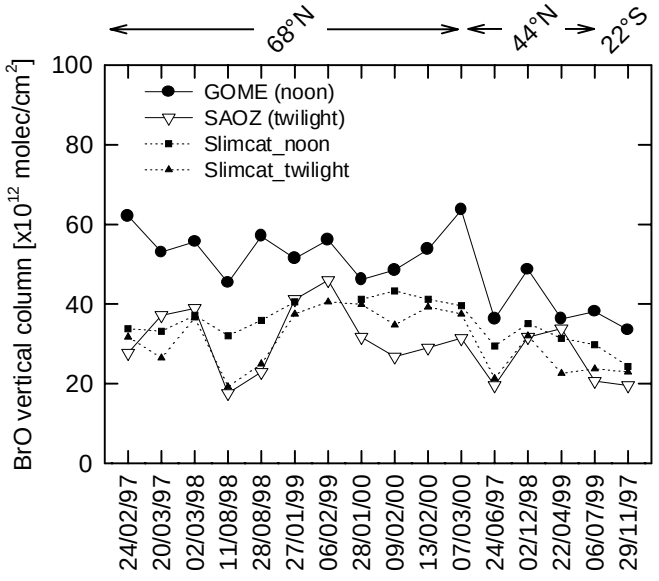

Fig. 1. BrO integrated stratospheric profiles measured at different latitudes and seasons using the SAOZ-BrO balloon instrument, in comparison to GOME column measurements and SLIMCAT 3D model simulations.

These results suggest, as previously proposed by Platt (1997), that significant amounts of BrO

could be maintained in the troposphere in all seasons and over extended latitudinal regions. This large-scale tropospheric BrO background would add up to the now established boundary layer BrO produced in spring over polar regions (Wagner and Platt, 1998; Richter et al., 1998). However this interpretation has to be questioned because (1) it relies heavily on the accuracy of the GOME BrO retrieval, and (2) the current knowledge of the tropospheric chemistry do not easily provide the mechanisms that would explain the presence of significant amounts of activated bromine in the free troposphere. Therefore, in order to rule out the possibility of a bias in the GOME BrO retrieval, further evidences have to be identified. The issue is double, validating GOME and demonstrating or invalidating the free-tropospheric BrO hypothesis. In the next part, recent findings addressing these issues based on balloon-borne and more particularly ground-based measurements are presented.

Although balloon-borne solar occultation instruments are by design best suited for profile measurements in the stratosphere, the possibility to extend the technique to tropospheric observations has been investigated by the SAOZ-BrO and LPMA/DOAS teams. In a recent study, Fitzenberger et al. (2000) describe first successful profile

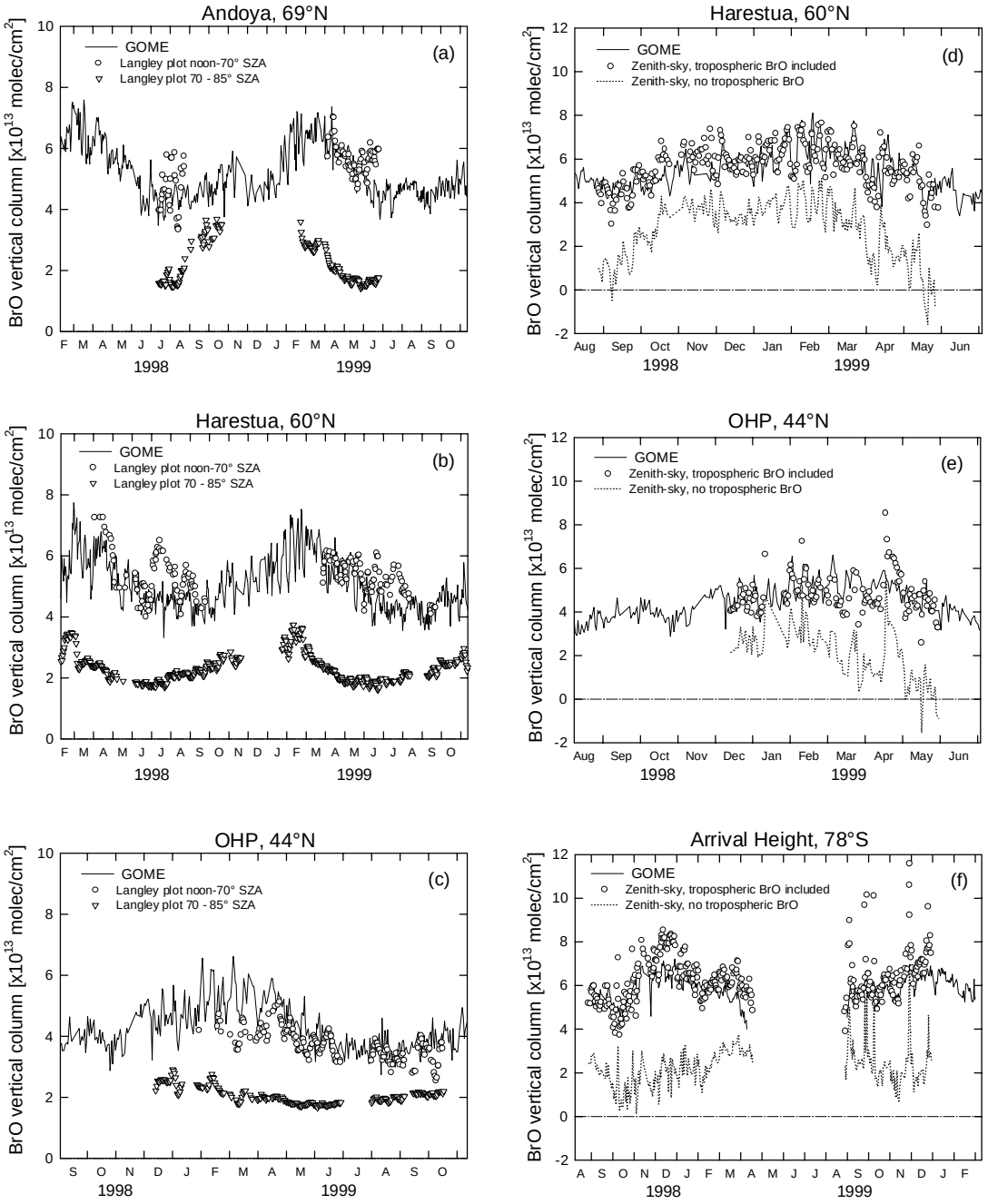

Fig. 2. GOME BrO vertical columns calculated in 500 km radius around indicated ground-based stations, compared to vertical columns derived from zenith-sky data by a Langley plot method (left panel) or from noon "GOME overpass" analyses using a seasonal reference spectrum (right panel).

measurements of tropospheric BrO obtained from Kiruna (67°N) using the LPMA/DOAS instrument. For technical reasons the reported observations are unfortunately limited to two flights where the data analysis effectively reveals significant concentrations of BrO in the free troposphere. These results are shown to be consistent with GOME column measurements on the same days (Fitzenberger et al., 2000), and not inconsistent with SAOZ balloon observations performed in similar conditions. However the smaller sensitivity of this latter instrument currently prevents actual confirmation of the LPMA/DOAS results.

In principle ground-based total column measurements should allow more direct comparisons with GOME than balloon measurements. In practice, however, difficulties arise due to the fact that (1) absolute slant columns cannot be obtained directly with ground-based instruments, and (2) ground-based observations are usually made at twilight to optimise their sensitivity (to the stratosphere), while GOME measures at noon. The conversion of BrO differential slant columns to vertical columns as needed for comparison with GOME is also complicated by the photochemical change of BrO during the day.

In first attempt estimations of the BrO vertical column were obtained using Langley plots. In this method, a linear relationship between airmass factor and slant column is assumed and the vertical column is derived from the slope of the correlation curve. Langley plot slopes are in principle independent of the choice of the reference spectrum, which can therefore be changed every day minimising the impact of instrumental instabilities. However in the case of BrO the vertical column is not constant with time which means that (1) the results depend on the range of solar zenith angle values included in the analysis, and (2) the accuracy of the vertical column determination is severely limited. Figures 2a,b,c show Langley plot and GOME BrO vertical columns calculated over three stations of the network (Andoya, Harestua and OHP). Langley plot evaluations are given in two ranges of solar zenith angles. As can be seen, columns obtained during twilight when the method is mostly sensitive to the stratosphere are systematically smaller than columns derived at lower solar zenith angles. Langley plot "noon" evaluations are qualitatively consistent with GOME, which together with previous results is clearly an indication for the presence of BrO in the troposphere.

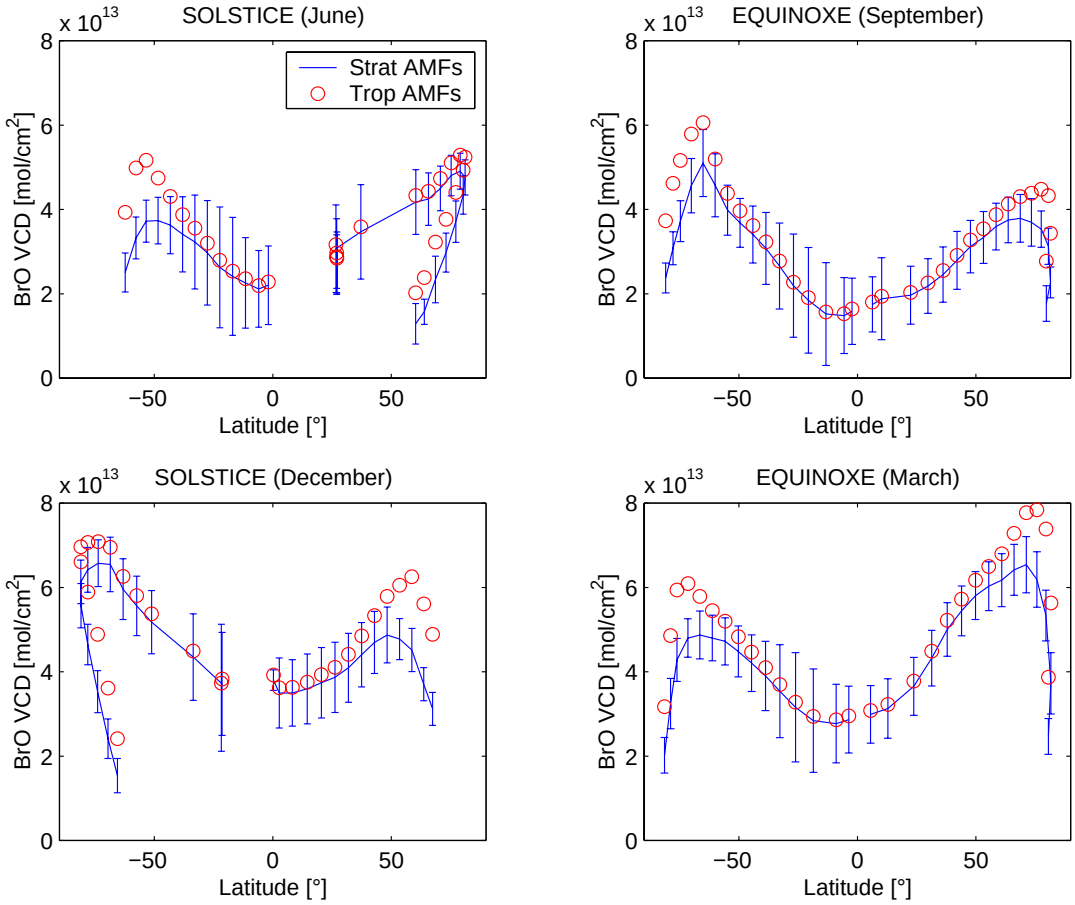

Fig. 3. Zonal means of GOME BrO vertical columns calculated over 10-days periods around solstices and equinoxes in 1998, and sorted by bins of 5° of solar zenith angle. The error bars represent the variability of the column within each bin (1σ). Open circles denote results obtained using airmass factors including tropospheric BrO (see text).

As already stated, however, Langley plot BrO columns are uncertain, especially at high sun, and possibly biased by the diurnal variation. Alternatively, BrO vertical columns can be derived at the time of the GOME overpass using a single seasonal reference spectrum (Wagner, 1999). This approach is potentially more accurate, but requires good instrumental stability over suitably long periods of time, which is not easily achieved by all instruments. Moreover the amount of BrO in the reference spectrum has to be determined. Results obtained in Harestua, OHP and Arrival Height are displayed in Figures 2d,e,f. Again two evaluations are given for the ground-based data. These correspond to different assumptions for the amount of BrO in the reference spectrum. In the case denoted by open circles, a tropospheric contribution consistent with the GOME column has been assumed. Note the convincing agreement with GOME, especially in terms of day-to-day variations. In the second case (dotted line), the amount of BrO in the reference spectrum has been infered from the SLIMCAT model (no tropospheric BrO). It is obvious that these latter results display unrealistically small values in late spring.

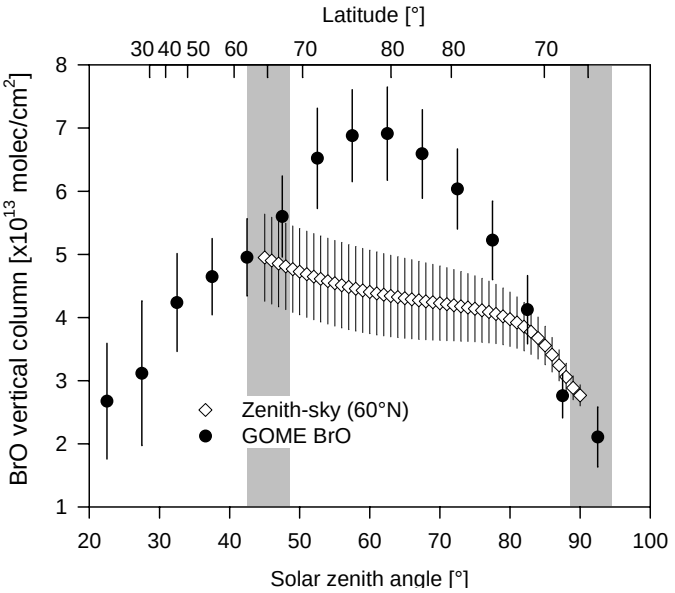

Fig. 4. GOME BrO zonal means calculated over a 10-days period in May 1998, compared to ground-based measurements from Harestua (60°N) averaged over the same period. The reduced GOME BrO columns at large solar zenith angle are consistent with the BrO diurnal variation inferred from ground-based data.

In brief, it can be concluded from the above results that the presence of a large scale background of tropospheric BrO above regions of mid- and high latitudes in both hemispheres appears to be strongly supported by GOME observations and by correlative data, both from balloon and from the ground. The existence of a tropospheric BrO background has direct consequences on the accuracy of the GOME BrO product because of the different behaviours of tropospheric and stratospheric airmass factors. A qualitative estimation of the impact of including a tropospheric component in the GOME BrO airmass factors is given in Figure 3, for GOME BrO zonal averages calculated around solstices and equinoxes in 1998. Although the tropospheric correction applied here is rather crude, corresponding to a fixed BrO profile with a troposphere to stratosphere column ratio of one, regions (mostly of high latitudes) and periods of time where the accuracy of the GOME BrO airmass factor is an issue are clearly apparent.

Another interesting feature revealed by Figure 3 is the behaviour of GOME BrO columns above polar regions during summer. In these conditions, GOME samples the same latitudinal region twice an orbit first at twilight and later at noon. Whatever the airmass factor used, BrO columns are always found to be smaller over the “slant pixels”, likely due to chemical conversion of BrO at twilight. This interpretation is tested on a more quantitative basis in Figure 4 where GOME and ground-based data (60°N), averaged over the same period and retrieved using similar assumptions (i.e. airmass factors including tropospheric BrO but no correction for chemical enhancement along the light path), are plotted together as a function of the solar zenith angle. Shaded areas roughly indicate the regions where GOME and ground-based measurements show reasonable overlap. As can be seen, the reduction of the GOME BrO column at large solar zenith angle appears to be consistent with the BrO diurnal variation inferred from the ground-based data.

CONCLUSION

The consistency between BrO column and profile measurements from three different platforms (GOME, balloon and ground-based) has been investigated during the European THESEO campaign (1998-1999). In agreement with recent findings (Harder et al., 1998, Van Roozendael et al., 1999, Pundt et al., 2000) it is found that BrO total columns measured by GOME significantly exceed the stratospheric amounts that can be inferred from other sources. Adding to the recently published balloon results of Fitzenberger et al. (2000), ground-based data evaluated at noon in time coincidence with GOME measurements strongly suggest that a large-scale background of tropospheric BrO do exist in all seasons in the mid- and high latitude free-troposphere. The sources of this tropospheric BrO are still to be established. Although a significant contribution probably comes from the transport of BrO plumes produced in the PBL of both polar hemispheres in spring (Wagner and Platt, 1998), it is unlikely that this mechanism can sustain large amounts of BrO over mid-latitudes in all seasons. Alternatively a production

mechanism involving the inorganic bromine existing in the free-troposphere could be searched as proposed by Pfeilsticker et al. (2001). Further work is definitely needed to better characterise atmospheric BrO from space, balloon and ground-based platforms.

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