

## Stratospheric BrO profiles measured at different latitudes and seasons: Atmospheric observations

H. Harder<sup>3,1</sup>, C. Camy-Peyret<sup>2</sup>, F. Ferlemann<sup>1</sup>, R. Fitzenberger<sup>1</sup>, T. Hawat<sup>2</sup>,  
H. Osterkamp<sup>1</sup>, M. Schneider<sup>1</sup>, D. Perner<sup>3</sup>, U. Platt<sup>1</sup>, P. Vradelis<sup>1</sup>, and K.  
Pfeilsticker<sup>1</sup>

**Abstract.** Stratospheric BrO profiles were measured at different latitudes and in different seasons in 1996/97 during three flights of the LPMA/DOAS balloon gondola (LPMA/Laboratoire Physique Moléculaire et Application and DOAS/Differential Optical Absorption Spectrometry). Using direct sunlight DOAS spectrometry the following BrO mixing ratios were measured; (1) 9 to 14 ppt in the height range from 20 to 30 km (at solar zenith angles, SZA < 88°) during ascent, (2) about (14 ± 2) ppt for altitudes above the balloon float altitude at 30.6 km, 30.0 km, and 39.8 km, and (3) 5 to 10 ppt in the 20-30 km region during sunset. The lower BrO concentrations during sunset than those observed prior at daytime indicate a conversion of BrO into nighttime reservoir species (BrONO<sub>2</sub>, HOBr, and BrCl). The overall agreement of our UV spectroscopic BrO profiles with recent measurements using the chemical conversion/resonance fluorescence technique is good. Our BrO profiles are also in reasonable agreement with the present stratospheric Br<sub>y</sub> burden and chemistry. Conversely collocated ground-based and satellite column measurements, however, show significantly more total atmospheric BrO (50 - 100%) than the integrated stratospheric BrO balloon profiles can account for. This indicates a global tropospheric BrO background, estimated at 1 - 2 ppt.

### 1. Introduction

In the lower stratosphere bromine is photochemically released from source gases (CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, CBrClF<sub>2</sub>, CBrF<sub>3</sub>,...) which presently amount to 19 ± 1 ppt in total Br<sub>y</sub> [Wamsley et al., 1998; Schauffler et al., 1998]. After release Br is present in inorganic form (BrO, Br, Br<sub>2</sub>, BrCl, BrONO<sub>2</sub>, HOBr, and HBr known collectively as Br<sub>y</sub>). Due to the lower binding energy of HBr compared to HCl and to the more rapid photolysis of Br<sub>2</sub>, BrCl, BrONO<sub>2</sub>, and HOBr compared to their Cl analogs about half of the Br<sub>y</sub> consists of the active species Br and BrO during daytime [Lary et al., 1996a,b], whereas typically only a few percent of inorganic chlorine is present as ClO. Therefore, although much less abundant in the atmosphere (Br<sub>y</sub>/Cl<sub>y</sub> ~ 0.6%), Br<sub>y</sub> can remove O<sub>3</sub> at a rate comparable to that of chlorine. In-situ measurements of stratospheric BrO (most of these made by the chemical conversion/resonance fluorescence technique) are sparse, quite limited with respect

to space and time coverage, and restricted to low ambient pressures [Brune et al., 1988, 1989; Avallone et al., 1995; Mc Kinney et al., 1997]. Remote stratospheric BrO observations using the DOAS (differential optical absorption spectroscopy) technique with scattered sunlight or direct moonlight were performed more widely. Presumably because of the still limited accuracy (± 30%) of previous measurements the BrO observed by both techniques apparently agree with expectations based on photochemical model calculations. Some studies, however, found a disagreement with our present understanding of the stratospheric BrO chemistry [Wahner et al., 1990; Butler et al., 1995; Otten et al., 1998].

For example, Wahner et al. [1990] reported nighttime stratospheric BrO in the wintertime activated arctic vortex (where Cl activation is expected). They interpreted this observation as an indication for different vertical concentration profiles of ClO and BrO, since the rapid conversion of BrO by reaction with ClO into BrCl would otherwise remove BrO from the nighttime stratosphere. More recently, stratospheric BrO measured on the ER-2 [Butler et al., 1995] indicated a total stratospheric bromine burden closer to 25 ppt than to 20 ppt. In addition, a comparison of ground-based measurements of BrO at Kiruna/Sweden in winter 1994/95 with photochemical calculations of the SLIMCAT model [M. Chipperfield, priv. comm.] showed a significant deficit (30%) in the modelled compared to the observed slant column density of BrO (SCD) at high stratospheric NO<sub>2</sub> concentrations during twilight [Otten et al., 1998]. BrO profiles measured by balloon-borne DOAS (SAOZ) over northern Sweden in winter 1997 showed good agreement with photochemical model calculations, except for 20 March 1997 when in the height range from 17 km to 25 km up to 30% more BrO was measured than modelled [Pundt, 1997].

Here we report on UV spectroscopic BrO profile measurements performed with the LPMA/DOAS balloon gondola during flights conducted at mid-latitude during fall (León/Spain, Nov. 23, 1996; flight 1) and summer (Gap/France, June 20, 1997; flight 3) and at high northern latitudes in winter (Kiruna/Sweden, Feb. 14, 1997; flight 2).

### 2. Observations

For the measurement of stratospheric profiles of O<sub>3</sub>, NO<sub>2</sub>, O<sub>4</sub>, BrO, NO<sub>3</sub>, H<sub>2</sub>O, and possibly CH<sub>2</sub>O, and IO, a novel DOAS-instrument (and two NO<sub>2</sub> photolysis sensors) were installed on the LPMA gondola. For details of the gondola see Camy-Peyret et al. [1993], and for the DOAS-instrument Ferlemann et al. [this issue, and 1998]. The combination of a UV/vis spectrometer with a Fourier transform infrared IR-instrument both performing solar occultation measurements offers several advantages: (1) Both instruments use the same infrastructure and the number of measured constituents is much larger (extending to HNO<sub>3</sub>, HCl, ClNO<sub>3</sub>, CH<sub>4</sub>, F11 ...), a comprehensive characterization of the chemical composition of the stratosphere is obtained. In the

<sup>1</sup> Institut für Umweltphysik, University of Heidelberg, Heidelberg/Germany

<sup>2</sup> Max-Planck-Institut für Chemie, Saarstr. 23, Mainz/Germany

<sup>3</sup> LPMA, CNRS, Université Pierre et Marie Curie, Paris/France

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**Table 1.** Overview of simultaneously performed ground-based, balloon-borne and ERS-2 satellite (GOME) BrO measurements.

Date and Time (UT)	Location	Range of SZA (degree)	Height Range (km)	Integrated BrO above the tropopause ( $10^{13}/\text{cm}^2$ )	Total atmospheric BrO-VCD	Comment	BrO above balloon float (i) (ppt)
Nov. 23, 96 14:55-16:52	León 42.6° N, 5 7° W	74-86.4 86.5-93.0 64.4	5.1-30.6 31.0-22.0 -	2.31 ± 0.45 - -	- 5.2 ± 2.2 -	Ascent Occultation GOME overpass	(14.4 ± 2.5) above 31.6 km total atmosphere
Feb 14, 97 12:19-14:49	Kiruna 67 9° N, 21.1° E	82.5-88.8 88.9-94.1 80.6 80.7	5.8-28.8 30.0-13.0 - -	3.99 ± 0.6 - - -	- 7.5 ± 2.0 6.5 ± 1.8 -	Ascent Occultation GOME (13 Feb. 97) ground-based	(15.5 ± 2.8) above 30.0 km - -
June 20, 97 3:30-7:42	Gap 44.0° N, 6.1° E	90.0-55.9 94.8-90.0	39.8-31.4 17.3-39.7	- -	- -	Descent Occultation	(15.3 ± 2.8) above 39.6 km

(i) Average mixing ratio (as determined from a linear regression of measured SCD of BrO versus total air slant column in the line of sight for SZA < 90°, see text) above balloon float altitude.

case of O<sub>3</sub> and NO<sub>2</sub> a cross validation is also possible.

#### Balloon Flights:

Three successful balloon flights were performed in 1996/97 (Table 1).

During flight 1 on Nov. 23, 1996, over northern Spain at ~39°N, direct Sun spectra were collected during balloon ascent (5 km to 30.3 km altitude) and during sunset to a tangent height of ~21.7 km.

Flight 2 on Feb. 14, 1997, over northern Scandinavia (68°N) followed a similar pattern and spectra in air-masses just outside the arctic vortex were collected. A triple blind test of O<sub>3</sub> and NO<sub>2</sub> among the DOAS, LP-MA, and ILAS instrument, the latter operated on the Japanese ADEOS satellite, showed an overall agreement of better than 10% (mixing ratio).

Flight 3 on June 20, 1997 over southern France (42° N) was launched at night and aimed at the investigation of the mid-latitude summer O<sub>3</sub> chemistry at dawn. The sun-tracker caught the solar disk at a tangent height of 2 km located over northern Switzerland, while the balloon was flying at an altitude of 40 km over the Rhone valley (42° N). Direct Sun measurements were continued during the slow balloon descent until 31.4 km (SZA of 55.9°) (Table 1). The tropospheric part of the measurements are reported elsewhere.

During each flight about 1000 spectra were recorded and analyzed.

### 3. Results

Vertical BrO profiles were derived from two observation modes, namely from balloon ascent and from solar occultation at float (Fig. 1a, and Fig. 1b). Note, that for flight 3 due to the incomplete descent a day profile could not be derived, but accurate BrO-SCD for the altitudes above balloon float (> 39.8 km) [Ferlemann *et al.*, this issue].

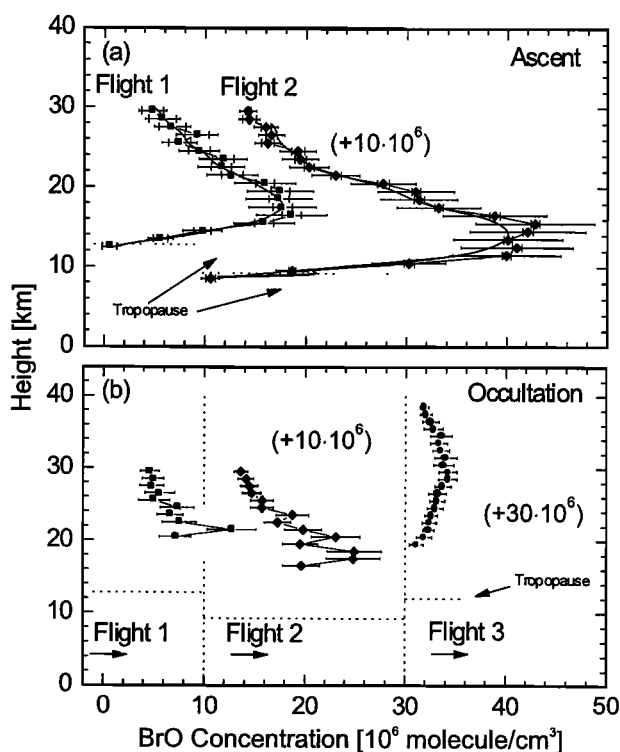
In the retrieved profiles photochemical processes causing spatial and temporal variations of the stratospheric BrO during the measurements were not corrected for, mainly because of uncertainties in the stratospheric BrO chemistry.

Since the onion peeling and the matrix inversion profile retrieval techniques [Ferlemann *et al.*, this issue] react differently on photochemical changes the overall consistency in the retrieved BrO profiles using both inversion techniques (Fig. 1a) suggests only small errors of the ascent profiles due to photochemistry. In addition, from a comparison of measured and modelled ground-based BrO-SCDs, Frieß *et al.* [1998] concluded to a negligible photochemical change in BrO for SZA < 86°. In contrast photochemical corrections, estimated to 10% to 20% in our case [Roscoe and Pyle, 1987], are certainly to be taken into account for the solar occultation observations (Fig. 1b).

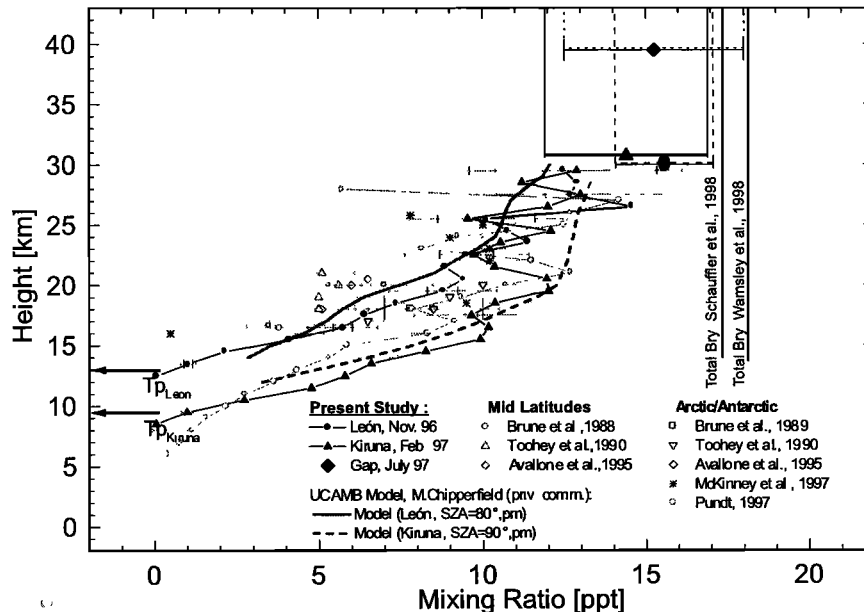
All BrO profiles show a strong increase of BrO mixing

ratios up to 18 km. This is expected, since inorganic Br<sub>y</sub> released from its organic precursors [Wamsley *et al.*, 1998] and most part being present in BrO during daytime [Lary *et al.*, 1996a,b].

For both afternoon ascents (flights 1 and 2), BrO volume mixing ratios were in the range of 9 ppt to 15 ppt in the lower stratosphere (20 km - 30 km). During solar occultation (Fig. 1b) only about 50% of the BrO is found at the corresponding altitudes (Fig. 1a). This manifests the BrO conversion (through reaction with NO<sub>2</sub> and HO<sub>2</sub>) into the bromine nighttime reservoir species BrONO<sub>2</sub> and HOBr (and less important into BrCl, sin-



**Figure 1.** Vertical profile of BrO measured during flights 1, 2, and 3. (a) BrO concentration ( $1/\text{cm}^3$ ) versus height for the balloon ascents. Note that for flight 3 no descent profile was measured (see text); (b) same as (a) but for the solar occultation measurements (for better visibility the profiles of flight 2 and 3 are shifted in steps of  $15 \times 10^6/\text{cm}^2$  against the profile of flight 1). The profiles including the error bars were calculated using the inversion technique, and the profile drawn by a full line is derived with the onion peeling technique.



**Figure 2.** Comparison of our measured stratospheric BrO profiles with those being previously reported (for details see text). Note that the BrO values of *Brune et al.* [1988, 1989], *Toohey et al.* [1990], and *Avallone et al.* [1995] were recently revised (D. Toohey, priv. comm.). For comparison modelled BrO profiles [M. Chipperfield, priv. comm.] calculated for our conditions are also shown.

ce chlorine activated airmasses were not encountered during the flights).

Likewise, at sunrise near summer solstice at mid-latitudes (flight 3) BrO mixing ratios are lower than for both winter sunset occultations below 23 km. This is a consequence of a more efficient formation of BrONO<sub>2</sub> (and subsequently heterogeneous formation of HOBr) due to the then larger stratospheric NO<sub>2</sub> abundance. All balloon float observations at SZA < 90° (in fact 86.4° for flight 1 and 88.8° for flight 2) show the retrieved SCD of BrO to fall on a straight line with respect to the SCD of the probed air long the line of sight (see Fig. 3 in *Ferlemann et al.*, this issue). This behaviour is primarily because for altitudes above the balloon float BrO rapidly goes into a photochemical steady state with Br and less important BrONO<sub>2</sub> for SZA < 90° [M. Chipperfield, priv. comm.]. Assuming a uniformly distributed BrO in the air column above the balloon at float, our observations suggest BrO mixing ratios of (13.6±2.1) ppt and (15.0±2.3) ppt above 30 km for flights 1 and 2, respectively, and (15.3±2.8) ppt above 39.8 km flight 3 (Table 1, last column).

#### 4. Discussion of the BrO Measurements

A compendium of several stratospheric BrO mixing ratio profiles including ours is given in Figure 2. These data and the integrated BrO-VCDs are discussed in the following.

**Comparison with GOME BrO-VCDs:** A comparison between our integrated BrO profile measured from flight 1 and BrO-VCD from GOME (Table 1) which were recorded in rather good space and time coincidence (a set of 9 spectra measured at 42.4° N, 21° W on UT 12:27 and a SZA=63.8°) yields BrO-VCDs (2.3±0.45)×10<sup>13</sup>/cm<sup>2</sup> for the balloon, and (5.2±2.2)×10<sup>13</sup>/cm<sup>2</sup> for the GOME measurement. Unfortunately, such a direct comparison is not possible for flight 2 since on this day the GOME instrument was in a servicing phase. However, the day before, GOME measured (7.5±2.0)×10<sup>13</sup>/cm<sup>2</sup> over northern Scandinavia much larger than the integrated balloon BrO profile of (4.0 ± 0.6) × 10<sup>13</sup>/cm<sup>2</sup> above the tropopause.

#### Comparison with ground-based measurements:

Our ground-based DOAS-instrument installed at Kiruna measured a BrO-VCD of (6.5±1.8)×10<sup>13</sup>/cm<sup>2</sup> (T. Wagner, and F. Enell, priv. comm.), which is in reasonable agreement with the GOME measurement but is also larger than our integrated balloon ascent profile for flight 2.

From zenith sky observations of total BrO-SCDs performed at Kiruna in the late spring of 1995, *Otten et al.*, [1998] estimated a stratospheric BrO mixing ratio exceeding 15 ppt. This estimate was obtained by uniformly distributing the BrO-SCD measured from ground at low SZA (60°) into the stratospheric air column. In that study 'absolute' BrO-SCDs were derived from the ratio of the noon solar spectra and direct moon spectra recorded at night with the same instrument, and assuming negligible BrO for the nighttime stratosphere.

**Comparison with ER-2 measurements:** When comparing our spectroscopic measurement with the chemical conversion/resonance/fluorescence measurements (ER-2, balloon measurements of *Mc Kinney et al.*, [1997]) a possible ±10% systematic error due to the uncertainty of the BrO cross section has to be taken into account for our spectroscopic measurement [*Ferlemann et al.*, this issue]. On the other hand, a recent recalibration of the resonance/fluorescence instrument suggests 20% to 40% larger BrO concentration than reported previously (D. Toohey, priv. comm.). Accordingly, the BrO mixing ratios reported by *Brune et al.* [1988, 1989], *Toohey et al.* [1990], and *Avallone et al.* [1995] were corrected for in Figure 2 (D. Toohey, priv. comm.). Additionally accounting for the increase in total stratospheric Br<sub>y</sub> since the late 80's [*Wamsley et al.*, 1998], the previously conducted ER-2 BrO measurements are in good agreement with our observations (Fig. 2).

**Comparison with balloon profile measurements:** Since we are not aware of any BrO profile measurements conducted in the photochemically unperturbed mid-latitude middle stratosphere, a direct comparison for the flights 1 and 3 is not possible.

Flight 2 can be compared with a profile measured on 3 Feb. 1995 using the chemical conversion/resonance

fluorescence technique [Mc Kinney *et al.*, 1997]. Although measured in the cold chlorine activated arctic vortex, the in-situ BrO levels  $\sim (10 \pm 2)$  ppt in the height range from 17 km to 27 km agree well with our observations.

Furthermore, although conducted in different geophysical conditions our measurements compare reasonably well (within 20%) with the recent spectroscopic BrO profile measurements of the SAOZ-instrument [Pundt, 1997].

#### Comparison with photochemical model calculations:

Finally, we compare our BrO profile with expectations based on photochemical model calculations [M. Chipperfield, priv. comm.] for "averaged" solar illumination conditions (SZA=80° and 90°, respectively) encountered during flights 1 and 2. Although the modelled profiles can only be regarded as "proxies" for the observed profiles, both compare quite well. This indicates a reasonable agreement between the observation and the assumed amount of Br<sub>y</sub> and the adopted bromine photochemistry in the model. In turn, the agreement also reveals that photochemical changes of BrO during the ascent measurements are negligible. A more detailed comparison including the occultation measurements, however, will be presented in a forthcoming paper.

Finally it is evident that since the BrO profiles measured with either of the balloon-borne techniques agree among themselves and also with the photochemical model, but the integrated BrO profiles are clearly lower than the BrO-VCD measured with optical 'remote sensing' technique operated at ground, or from satellite. Thus a "missing" tropospheric BrO background has to be postulated. The comparison among the measurements suggests that already 1 - 2 ppt of uniformly distributed BrO in the troposphere would be sufficient to solve the discrepancy.

## 5. Conclusion

Our BrO profile measurements at different latitudes and seasons agree remarkably well with the recent in-situ BrO profile measurements of Mc Kinney *et al.*, [1997], although both sets of measurements were performed with different techniques under different geophysical conditions (for which, however, photochemical models do not predict much different BrO profiles). Although not yet performed in detail for all investigated conditions, our BrO profiles also agree apparently with photochemical model predictions of stratospheric BrO. A quite puzzling result is that the integrated stratospheric BrO profiles measured with both techniques are significantly lower than the total atmospheric BrO-VCDs measured with the spectroscopic 'remotely sensed' (ground-based and satellite). From this discrepancy we propose a 'global' tropospheric BrO 'background' of 1 - 2 ppt of BrO uniformly distributed into the troposphere.

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Harder et al., Institut für Umweltp Physik, Universität Heidelberg, D-69120 Heidelberg, Germany (e-mail harder@mpch-mainz.mpg.de)

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