

First Profile Measurements of Tropospheric BrO

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Abstract. Tropospheric BrO profiles (about 0.6 ± 0.2 ppt, and 2.0 ± 0.8 ppt at profile maximum) were measured for the first time. Our measurements add new information to recent speculations - based on indirect evidence - of BrO possibly being ubiquitous in the free troposphere [Harder *et al.*, 1998; Frieß *et al.*, 1999; Van Roozendael *et al.*, 1999; Pundt *et al.*, 2000]. Our study relies on a detailed comparison of BrO slant column densities (BrO-SCD) measured in the troposphere from the LPMA/DOAS (Laboratoire de Physique Moléculaire et Applications and Differential Optical Absorption Spectroscopy) gondola by direct Sun absorption, and BrO-SCD values subsequently measured in the lowermost stratosphere during balloon ascent. The difference in total atmospheric BrO-SCDs measured in the troposphere and lowermost stratosphere - after a suitable correction for the change in BrO due to photochemistry and the observation geometry - is then attributed to tropospheric BrO.

1. Introduction

Recent spectroscopic observations of tropospheric BrO have clearly established the role inorganic bromine plays in the destruction of planetary boundary layer (PBL) ozone during polar spring. The detection of PBL BrO - with mixing ratios up to 100 ppt - was based on either ground based long path absorption measurements [Hausmann and Platt, 1994], aircraft-borne backscattering UV/vis absorption measurements [McElroy *et al.*, 1999], and/or satellite-borne spectroscopy [Wagner and Platt, 1998]. Also, our group recently recorded sizeable amounts of BrO [up to 80 ppt] emitted from salt pans located at the Dead Sea, Israel [Hebestreit *et al.*, 1999]. Speculations as to whether BrO ubiquitously occurs in the free troposphere not just during these specific BrO events - and thus influences the chemistry of tropospheric ozone - was prompted by a series of recent indirect evidence for BrO being possibly ubiqui-

tous in the free troposphere (about 1 - 2ppt, or $1-2 \times 10^{13}$ molecules/cm² in total atmospheric column). These studies relied on: (1) a comparison of collocated ground-based, balloon-borne, and satellite-borne (Global Ozone Monitoring Experiment, GOME) BrO observations, where discrepancies between the integrated stratospheric BrO profiles (measured from balloons), and the total atmospheric BrO column (measured from the ground and/or satellite) were found [Harder *et al.*, 1998; Van Roozendael *et al.*, 1999; Pundt *et al.*, 2000], and (2) a comparison between measured ground-based BrO-SCD, and model (SLIMCAT) predicted stratospheric BrO profiles where the model - accounting for 20 ppt of total stratospheric inorganic bromine [e.g., Schauffler *et al.*, 1998; Wamsley *et al.*, 1998; Harder *et al.*, 2000] - significantly underpredicted the total atmospheric BrO column amount measured around local noon [Frieß *et al.*, 1999].

Here, we report on first BrO profiles measured by direct Sun DOAS spectroscopy that were conducted from aboard the azimuth-angle-controlled LPMA/DOAS balloon payload.

2. Methodology and Measurements

The balloon-borne UV/vis DOAS spectroscopy technique aims at the profile measurements of BrO, OClO, NO₂, O₃, O₄, IO, and some other gases. More details of the technique can be found in Ferlemann *et al.* [1998, 2000], and Harder *et al.* [1998, 2000].

The small atmospheric absorption of BrO (typical optical densities are $\sim 10^{-3}$ for the UV vibrational absorption bands 4-0 at 354.7 nm, and 5-0 at 348.8 nm of the $A(^2\Pi) \leftarrow X(^2\Pi)$ electronic transition) are spectroscopically monitored by applying the DOAS-technique [Platt, 1994] to direct Sun spectra collected with a Sun tracker mounted on the azimuth-angle-controlled LPMA/DOAS balloon gondola. Direct Sun tracking - rather than using a diffuser for diffuse sky and direct Sun light collection - is essential for a thorough direct detection of tropospheric BrO, since it establishes a well defined light path in the troposphere [e.g., Harder *et al.*, 2000]. The Sun spectra are analyzed within a pressurized, and thermally stabilised, grating spectrometer [Ferlemann *et al.*, 2000]. This avoids unwanted spectral shifts and squeezes due to the changing refractive index caused by changing ambient pressures, as well as thermally induced misalignments of the optical set-up. The precision ($\pm 4\%$), and accuracy ($\pm 12\%$ plus $\pm 5 \times 10^{12}$ molecules/cm²) of our stratospheric BrO-SCD measurements are discussed in detail by Ferlemann *et al.* [1998, 2000], and Harder *et al.* [1998, 2000].

Eight LPMA/DOAS balloon flights have already been successfully conducted at mid- and high latitudes during all seasons (Table 1). Since the detection of tropospheric BrO essentially relies on a subtraction of sequentially measured tropospheric and stratospheric BrO-SCDs during balloon ascent - after accounting for the photochemical change in the stratospheric BrO con-

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Table 1. Compendium of simultaneously measured BrO-VCDs by Balloon (LPMA/DOAS), Satellite (GOME), and Ground-Based (GB)

No	Date	Location	SZA [°]	Altitude [km]	BrO-VCD above Tropopause (10^{13} molec./cm ²)	BrO-VCD (10^{13} molec./cm ²)	GOME SZA [°]	BrO above H _{float} [ppt]
1.	Nov. 23, 96	León (42.6° N, 5.7° W)	74 – 86.4	12 – 30.6	2.3 ± 0.5	4.3 ± 0.8 (GOME) 6.0 ± 1.0 (GOME)	65.4	14.4 ± 3
2.	Feb. 14, 97	Kiruna (67.9° N, 21.1° E)	82.5 – 88.8	8 – 30	4.0 ± 0.6	6.8 ± 0.8 (GOME, Feb. 13) 6.4 ± 2.0 (GB)	81.7	15.6 ± 3
3.	Jun. 20, 97	Gap (44.0° N, 6.1° E)	90 – 56	39.8 – 31	–	5.2 ± 1.0 (GOME)	23.4	15.3 ± 3
4.	Mar. 19, 98	León (42.6° N, 5.7° W)	65 – 87	5 – 38.5	2.0 ± 0.5	4.4 ± 0.5 (GOME)	45.5	12 ± 2
5.	Aug. 19/20, 98	Kiruna (67.9° N, 21.1° E)	74.8 – 87	2.2 – 38.5	3.2 ± 0.5	4.0 ± 0.5 (GOME) 3.6 ± 0.8 (GB)	55.6 75 – 87	17 ± 3
6.	Feb. 10, 99	Kiruna (67.9° N, 21.1° E)	82.9 – 86.2	0.2 – 28.2	4.8 ± 0.5	4.0 ± 0.5 (GOME) 5.7 ± 0.7 (GOME) 6.7 ± 0.8 (GB)	56.0 82.1	13 ± 2 13 ± 2
7.	Jun. 25, 99	Gap (44.0° N, 6.1° E)	93.5 – 50.0	39.1 – 20.5	–	3.3 ± 0.5 (GOME)	24.3	–
8.	Feb. 18, 2000	Kiruna (67.9° N, 21.1° E)	81.4 – 89.9	6 – 30.1	3.8 ± 0.5	5.5 ± 0.7 (GOME)	82	17 ± 2

centration and observation geometry (see below) - the method is only suitable if the resulting difference is larger than the combined uncertainties of both measured BrO-SCDs. It is thus necessary to discuss thoroughly the uncertainties involved in the method.

Unfortunately only two LPMA/DOAS balloon flights so far performed are suitable for a search for tropospheric BrO. First, sunrise occultation measurements (flights 3, 7, second part of flight 5) are conducted from the balloon flying in the mid- and upper stratosphere, and thus detection of tropospheric BrO is not possible. Second, strong tropospheric shear wind (flights 1, 2, and 4), technical problems and/or clouds (flight 8) prevented a proper Sun pointing during the tropospheric part of the ascent. Third, the solar zenith angle (SZA) - and thus the air mass factor under which the comparably small tropospheric and much larger stratospheric BrO columns are observed - are too small for some of the flights (1 and 4) to separate the small tropospheric from the larger stratospheric column. Therefore, we feel that

flight 6 (from Kiruna on Feb. 10, 1999) - with a large Signal-To-Noise ratio (SNR) - is most suitable for direct detection of the small tropospheric BrO concentrations. Tropospheric BrO can also be inferred from the flight 5 (Kiruna on Aug. 19, 1998), however, with a smaller SNR than for flight 6. Also the ascent measurements of flight 5 were partly affected by remnants of one of the auxiliary balloons that unfortunately engulfed parts of the balloon gondola, and thus eventually obscuring the telescope's view of the solar disc.

For flight 6, Figure 1 compares the measured and modeled BrO-SCD as a function of flight time. As the balloon ascends through the troposphere into the lower stratosphere, the BrO-SCDs remain nearly constant. Further on, the measured BrO-SCDs decrease strongly, particularly when the balloon passes the maximum height of the BrO concentration profile and then ascends further to the balloon float altitude (at 28 - 29 km, and SZA=86.2°). During solar occultation, the BrO-SCD values increase again, because the line of sight through the absorbing BrO layer becomes longer. The modeled BrO-SCDs are obtained by integrating photochemically modeled stratospheric BrO concentrations along the line of sight of our observation (for details see Figure 1 in *Harder et al.*, [2000]). The modeled SZA-dependent BrO concentration field is taken from the SLIMCAT 3D-CTM model for the closest grid point to our measurement [*Chipperfield*, 1999]. Clearly, the measured and modeled BrO-SCDs compare excellently for the observation after 12:30 UT (above 20 km), while an increasing gap opens between measured and modeled BrO-SCD with decreasing atmospheric height. While a part of the gap is due to a shortcoming of the SLIMCAT model to correctly predict lowermost stratospheric BrO concentrations for that flight, the remainder of the gap may possibly point to tropospheric BrO. Since a forthcoming paper - involving a comparison of total stratospheric bromine inferred from our BrO measurement, and a GC/MS analysis of total organic bromine in stratospheric air samples taken close to our flight [*Pfeilsticker et al.*, submitted to GRL, 2000] - will address the model's underprediction of lower stratospheric BrO in detail, we focus here on the tropospheric contribution to this gap.

A zoom of the low altitude intercomparison is also shown in Figure 1. All three simulations (curves 1, 2, and 3) describe the amount of BrO-SCD that would have been measured if there was only stratospheric BrO present. Curve 1 is a SLIMCAT simulation of stratospheric BrO for our flight. Curve 2 is calculated from the later on measured stratospheric BrO profile including no photochemical corrections. It has to be noted that assuming no photochemical related change in stratospheric BrO during the course of the measurements slightly underpredicts the BrO-SCD, mainly because during balloon ascent some of the stratospheric BrO (~4 %)

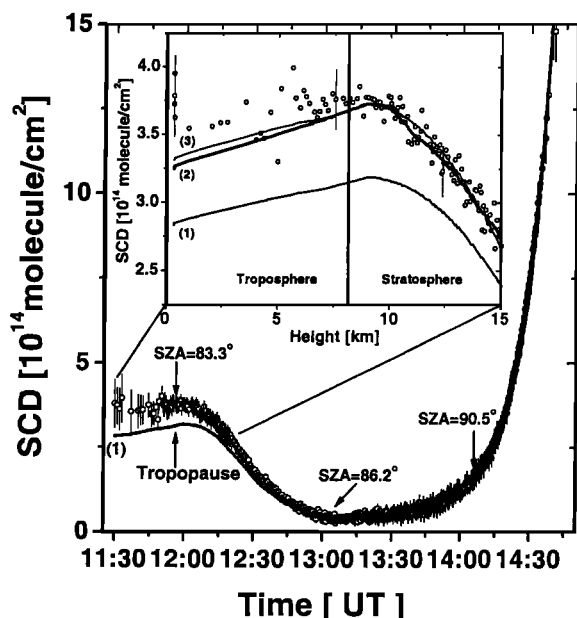


Figure 1. Comparison of measured and modeled BrO-SCDs for the balloon flight from Kiruna (67.9°N, 21.1°E) on Feb. 10, 1999 as a function of flight time. The modeled curves are simulated line of sight BrO-SCDs for (a) stratospheric BrO predicted by SLIMCAT (curve 1), (b) the stratospheric BrO profile as measured by our instrument without photochemical correction (curve 2), and (c) as (b) but including the photochemical correction (curve 3) (for details see text).

has already reacted into its nighttime reservoir species (believed to be mainly BrCl for this flight). In order to account for this photochemical loss in stratospheric BrO, simulation 3 was carried out. Here we corrected our measured stratospheric BrO profile with the model-predicted loss of stratospheric BrO during our measurements. The corrections are $\sim 4\%$ for the total atmospheric column (see also Figure 2 for the model-predicted change in stratospheric BrO for the near ground and the lowermost stratospheric observations at SZA = 82.8° , and 83.3° , respectively).

To consolidate this result, we conducted a statistical test of the difference in measured and modeled BrO-SCDs for the tropospheric observations (difference of the measured values to curve 3). The test clearly shows that, the combined measured tropospheric BrO-SCDs are on a 97.5% significance level larger than the predicted values. Therefore, we conclude that some BrO was present in the troposphere.

Another test for the presence of tropospheric BrO relies on a comparison of measured total atmospheric BrO vertical column density (BrO-VCD), and the integrated stratospheric profile. Our integrated stratospheric BrO profile yields $(4.8 \pm 0.5) \times 10^{13}$ molecules/cm².

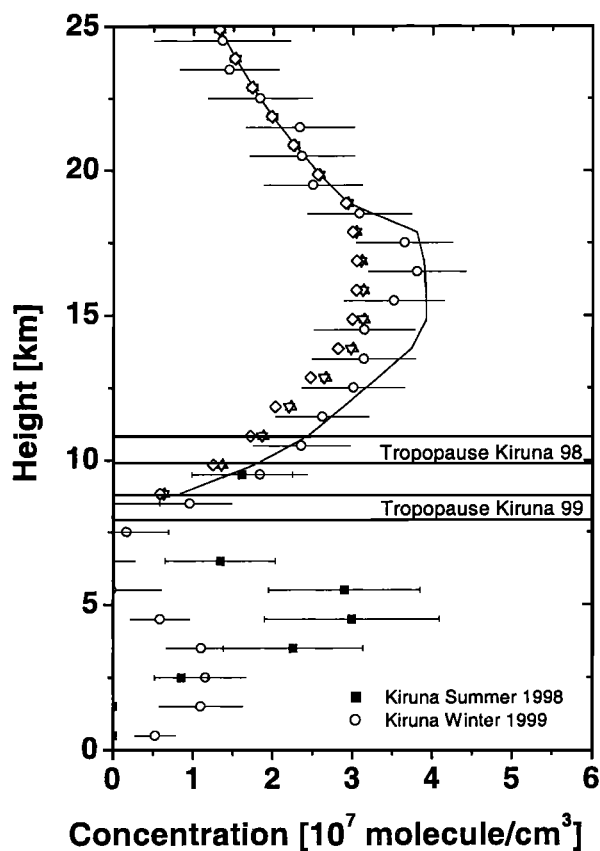


Figure 2. BrO profiles for the balloon flight from Kiruna on August 19/20, 1998 (dark squares), and Feb. 10, 1999 (open circle). The measured stratospheric BrO profile (open circle) is an average over $82.8^\circ \leq \text{SZA} < 86.2^\circ$ for the Feb. 10, 1999 flight. The modeled SLIMCAT profiles for grid point ($65^\circ\text{N}, 12^\circ\text{E}$) are for SZAs = 82.7° (open upper triangle), 86.2° (diamond), 83.3° (open lower triangle), corresponding to lower tropospheric, tropopause and float altitude measurement locations, respectively. The solid line shows the observation-corrected modelled BrO profile for an average SZA = 83° .

The measured total BrO-VCDs are taken from three sources: (1) the 4 combined BrO measurements - taken from the ground prior to the launch - result in a BrO-VCD of $(5.7 \pm 0.6) \times 10^{13}$ molecules/cm² for SZA = 82.8° , (2) GOME measured almost the same total atmospheric BrO-VCD of $(5.7 \pm 0.7) \times 10^{13}$ molecules/cm² for a similar SZA (= 82.2°) as for our balloon measurement, and (3) our ground-based instrument installed at Kiruna/Institutet för Rymdfysik (IRF), roughly 50 km from the balloon launch site, measured a BrO-VCD of $(6.7 \pm 0.8) \times 10^{13}$ molecules/cm² at a SZA = 82.2° . Combining all three measurements, then the combined atmospheric BrO-VCDs ($(5.9 \pm 0.4) \times 10^{13}$ molecules/cm²) as well as each of the individual total BrO-VCDs are significantly larger than the integrated stratospheric BrO profile. Finally, our integrated tropospheric profile results in a BrO column amount of $(0.5 \pm 0.2) \times 10^{13}$ molecules/cm², a value being in reasonable agreement with the above difference in the combined atmospheric BrO-VCD ($(0.2$ to $2.1) \times 10^{13}$ molecules/cm²), taking into account all errors. It has to be noted that our tropospheric BrO-VCD closely corresponds to the tropospheric BrO-VCD that is required to bring the measured total atmospheric and modeled stratospheric BrO-VCD into agreement for a comparison at the same location, and season, however, for 1995 [Frieß *et al.* 1999]. Finally, inspecting the inferred profile obtained for our balloon flight, the tropospheric BrO maximizes at around 2-3 km altitude (0.6 ± 0.2 ppt), and it is close to zero at the local tropopause (Figure 2).

In our search for tropospheric BrO, we also inspected closer flight 5. As before, the BrO-SCD values in the troposphere are larger than if there was only BrO in the stratosphere (not shown). For this flight - despite the smaller SNR for the measured BrO-SCDs because of smaller SZAs and hence line of sight air masses - weak shear winds allowed us to record occasionally spectra from 2.2 km altitude upwards. The inferred BrO profile (Figure 2) looks very similar to the winter profile (flight 6), however, with larger BrO mixing ratios at profile maximum (2 ± 0.8 ppt) than detected for flight 6. As before, comparing the total vertical column amounts - for the whole atmosphere, stratosphere, and troposphere - yields the following results (4.4 ± 0.5) , (3.2 ± 0.5) , and $(1.2 \pm 0.4) \times 10^{13}$ molecules/cm², respectively. A comparison of the values evidences that tropospheric BrO was also present during flight 5.

Table 1 summarizes our findings for the 8 LPMA/DOAS flights already conducted. The inter comparison reveals that tropospheric BrO - amounting to $(0.6$ to $3.7) \times 10^{13}$ molecules/cm², or 0.4 pptv to 2.3 pptv - if uniformly distributed within the troposphere - could have been present during all our balloon flights.

3. Discussion

We may speculate on the possible source of tropospheric BrO. For our measurement conditions, we can think of two potential sources; (1) BrO ventilated into the free troposphere from BrO plumes known to occur in the PBL of both polar hemispheres in spring, and early summer [e.g., Wagner and Platt, 1998], or (2) BrO transported from the stratosphere or photochemically produced from the destruction of bromine-bearing organic precursors in the troposphere [Dvortsov *et al.*, 1999]. At first glance, possibility 1 appears very appealing, because flight 6 was launched only about 400 km east of the Arctic Sea shores, and remnants of a BrO plume

formed there could easily be transported to Kiruna by westerly winds. However, plumes of BrO in the Arctic PBL are known to occur later in the season (by mid March), usually when the Sun rises over the Arctic sea ice belt located much more northerly (1500 km) than the balloon trajectory [e.g., Wagner and Platt, 1998]. Also, possibility 1 can hardly explain our BrO observation for flight 5 in late summer, and the evidence we, and others, found for tropospheric BrO occurring at mid-latitudes (c.f., see flight 1) and the Tropics [Pundt et al., 2000]. Possibility 2 also provides no straightforward explanation. Although it is evident that inorganic bromine may exist at a several ppt level in the free troposphere [Dvortsov et al., 1999], the gas phase bromine photochemistry, however, largely favors (by at least a factor of 10) the presence of HBr, HOBr, and BrONO₂ (through fast reactions of CH₂O, OH, HO₂, and NO₂ with BrO or Br), rather than BrO. Since there is no free tropospheric source known to provide inorganic bromine in excess of several ppt, an activation mechanism must exist therefore. We propose that in the sunlit troposphere BrO is produced by a heterogeneous activation of HBr, HOBr, and BrONO₂, possibly by reactions involving HCl taken up on tropospheric hydrometeors (ice crystals, water droplets) [e.g., Abbatt, 1994; Abbatt, and Nowak, 1997; Erle et al., 1998; Disselkamp et al., 1999]. The subsequent release of BrCl, fast BrCl photolysis, and the reaction of Br atoms with ozone may then form BrO in the sunlit troposphere. If this mechanism occurs, then a small BrO background (some ppt at most) may exist ubiquitously in the free troposphere, preferentially in the wake of tropospheric clouds.

4. Conclusions

First measurements of tropospheric BrO profiles are reported. Our observations largely support speculations based on recent findings [Harder et al., 1998; Frieß et al., 1999; Van Roozendaal et al., 1999; Pundt et al., 2000], that BrO is possibly ubiquitous in the sunlit free troposphere. We propose that in the sunlit troposphere BrO is produced by a heterogeneous activation of HBr, HOBr, and BrONO₂ on hydrometeors, and some subsequent gas phase reactions, a reaction sequence that keeps the tropospheric BrO mixing ratio at daytime on a several ppt level at most. Before the proposed process can be verified, however, more tropospheric BrO profile measurements are necessary, particularly in the Tropics, where the proposed mechanism is potentially most effective.

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