Global observations of stratospheric bromine monoxide from SCIAMACHY

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[1] The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) onboard the ENVISAT satellite provides for the first time a global view on stratospheric bromine monoxide (BrO). Here we focus on a 10 day period in September 2002. The BrO retrievals are compared with modeled BrO profiles, based on estimated inorganic bromine (Br_y) from CFC-11 retrievals by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on ENVISAT and the calculated BrO/Br_y ratio from a photochemical model constrained by SCIAMACHY NO_2 retrievals. The BrO observations are broadly consistent with our current understanding of stratospheric bromine chemistry and a total stratospheric bromine loading of 18 ± 3 pptv. Comparisons between the measured stratospheric BrO column and the simultaneously measured total BrO column from SCIAMACHY nadir observations suggest an average global background tropospheric BrO mixing ratio of 1.0 ± 0.5 pptv.
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1. Introduction

[2] Bromine compounds play an important role in the catalytic destruction of stratospheric ozone. Despite their importance, however, there are only few measurements of bromine compounds in the stratosphere. The only major inorganic bromine compound that has been measured previously in the stratosphere is bromine monoxide (BrO).

[3] Stratospheric BrO profiles have been measured by balloon borne UV-visible spectroscopy [e.g., *Pfeilsticker et al.*, 2000; *Pundt et al.*, 2002] and from in-situ resonance fluorescence spectroscopy [e.g., *Avallone et al.*, 1995]. SCIAMACHY allows now for the first time a global view of stratospheric BrO profiles.

[4] One important but still open question is, whether the stratospheric bromine loading is consistent with the known sources of bromine. A budget of the known organic bromine source gases for 2002 is summarized in Table 1. The largest contributors are methyl bromide (CH_3Br), which has both anthropogenic and natural sources, and the halons, which are purely anthropogenic. In addition, there could be significant contributions from short-lived bromine compounds, which are mainly of natural origin. Note that two of these short-lived compounds (CH_2Br_2 and CH_2BrCl) are already considered by the analysis of *Wamsley et al.* [1998], whereas others (e.g. bromoform, $CHBr_3$) are not. In particular bromoform could potentially make a significant contribution to the stratospheric bromine loading [*Sturges et al.*, 2000]. The modeling studies of *Dvortsov et al.* [1999] and *Nielsen and Douglass* [2001] both indicated that about 1 ppt of Br_y in the stratosphere may result from bromoform.

[5] In order to test whether the SCIAMACHY BrO observations agree with our current understanding of the stratospheric bromine chemistry we compare the measured BrO with modeled BrO profiles, based on Br_y derived from MIPAS CFC-11 using the empirical correlation of *Wamsley et al.* [1998] and the calculated BrO/Br_y ratio from a photochemical model constrained by SCIAMACHY retrievals of NO_2. In this study we focus on the ten day period from 18–27 September 2002, as this was one of the first periods for which extensive scientific data products from SCIAMACHY and MIPAS were retrieved.

2. Measurements and Data Analysis

2.1. SCIAMACHY BrO Measurements

[6] SCIAMACHY was launched on board ENVISAT in March 2002. It measures the scattered and reflected solar radiation in limb and nadir geometry in the spectral range from 240 to 2380 nm. ENVISAT is in a sun-synchronous orbit with an equator-crossing local time of about 10 AM and 10 PM. A detailed description of the instrument design and capabilities is given by *Bovensmann et al.* [1999].

[7] BrO profiles are retrieved from the SCIAMACHY measurements using the Uni Bremen retrieval processor version CDI-(V1.2.17-2) (www.iup.physik.uni-bremen.de/scia-arc) as described by *Rozanov et al.* [2005], and the temperature-dependent BrO absorption cross-sections from *Fleischmann et al.* [2004]. The BrO retrieval is possible in the altitude range from about 15 to about 30 km with a precision of about 30–50% for a single profile and an estimated systematic error of 10 to 20% or at least 1 pptv (including the contribution due to remaining pointing uncertainty, see below). A more detailed error analysis is given by *Rozanov et al.* [2005], including a first comparison of the SCIAMACHY BrO profiles with in-situ balloon borne BrO measurements. A more extensive validation of

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Table 1. Budget of Organic Bromine Source Gases for 2002

Source Gas		Mixing Ratio,[a] pptv	Reference
Included by Wamsley et al. [1998]			
Methyl bromide	CH_3Br	8.1	*Montzka et al.* [2003b]
Halon-1211	$CBrClF_2$	4.1	*Montzka et al.* [2003b]
Halon-1301	$CBrF_3$	2.6	*Montzka et al.* [2003b]
Halon-2402	$C_2Br_2F_4$	0.4	*Montzka et al.* [2003a]
Dibromomethane	CH_2Br_2	1.21 (0.9–1.5)	*Ko et al.* [2003]
Bromochloromethane	CH_2BrCl	0.14	*Wamsley et al.* [1998]
Total		18.16	
Not included by Wamsley et al. [1998]			
Halon-1202	CBr_2F_2	0.04	*Montzka et al.* [2003a]
Bromoform	$CHBr_3$	1.63 (0.9–2.3)	*Ko et al.* [2003]
Dibromochloromethane	$CHBr_2Cl$	0.16 (0.06–0.26)	*Ko et al.* [2003]
Bromodichloromethane	$CHBrCl_2$	0.19 (0.14–0.26)	*Ko et al.* [2003]

[a]For long-lived species global mean surface mixing ratios are given. For very short-lived gases the median and range of tropical boundary layer mixing ratios are given.

SCIAMACHY BrO is currently under way (M. Dorf et al., manuscript in preparation, 2005).

[8] One of the largest uncertainties for the BrO retrieval is imperfect pointing knowledge [*von Savigny et al.*, 2005]. For the results presented here the retrieval process includes a global tangent height offset of −1.5 km relative to the engineering tangent heights provided by the Level 1 data set. This offset is consistent with the mean tangent height offset during September 2002, as derived from SCIAMACHY tangent height retrievals [*von Savigny et al.*, 2005], as well as the mean tangent height offset retrieved from MIPAS measurements [*von Clarmann et al.*, 2003].

[9] Here we focus on zonally averaged BrO. BrO is averaged over the 10 day period in 5° latitude bins, with about 40 to 50 profiles per bin from a total of 1312 profiles. This reduces the error due to measurement noise to about ±5% (one sigma).

[10] One of the important and novel features of SCIAMACHY is the ability to observe the same air mass first in limb and thereafter in nadir-viewing geometry within about 7 minutes. Nadir BrO columns have been retrieved as described by *Afe et al.* [2004], similar to the GOME analysis [*Richter et al.*, 1998], but using the cross sections of *Fleischmann et al.* [2004] for consistency. The main error source of the nadir BrO columns is the uncertainty in the air mass factors. Satellite nadir measurements are much less sensitive to BrO in the lower troposphere than in the stratosphere [*Afe et al.*, 2004]. Any BrO contribution from the lower troposphere will therefore be underestimated, while BrO over bright clouds might be slightly overestimated. The spectral analysis and a possible bias from the irradiance spectrum used also contribute to the overall error, which is estimated to be 20% at mid and high latitudes and 30% in the tropics.

2.2. MIPAS CFC-11 Measurements

[11] CFC-11 profiles have been retrieved from MIPAS measurements as described by *Glatthor et al.* [2005]. 100 to 120 individual profiles from the period 18 to 27 September 2002 were averaged to create each zonal mean profile representing a 5° latitude bin, except for the 5 to 10°N and 80 to 85°N latitude bins where only about 60 profiles each were available. The total precision is estimated to be 5–17% in the lower stratosphere, while systematic error contributions which do not cancel out by zonal averaging amount to 4–15%.

[12] An estimate of Br_y is calculated from the MIPAS CFC-11 measurements using the empirical correlation of *Wamsley et al.* [1998]. Tropospheric source gas concentrations were taken as indicated in Table 1. This results in a total bromine loading of 18.16 ppt. As the total bromine loading was rather constant during the last few years prior to 2002 [*Montzka et al.*, 2003b], we did not consider a variation of the bromine loading with age of air.

[13] Note that our estimate of Br_y includes also the contribution from the two short-lived source gases CH_2Br_2 and CH_2BrCl, but not other short lived gases such as bromoform or any influx of Br_y from the troposphere. Thus, this estimate of Br_y may be considered a lower limit for the available inorganic bromine.

2.3. Model

[14] The photochemical model to calculate the expected BrO/Br_y ratio is a 1D-column model (stacked box model) based on the chemistry scheme from the SLIMCAT model [*Chipperfield*, 1999]. The model has a state-of-the-art treatment of stratospheric (bromine) chemistry. Reaction rate constants are taken from JPL-2002 recommendations [*Sander et al.*, 2002], unless otherwise noted.

[15] The model is initialized by the output of a two-dimensional (latitude-height) model [*Sinnhuber et al.*, 2003, and references therein]. Temperature and pressure profiles are taken from ECMWF analyses. As the NO_2 concentrations have an impact on the bromine partitioning, we have constrained the model by the SCIAMACHY NO_2 profiles by scaling NO, NO_2, NO_3, N_2O_5, and HNO_3 (but not $ClONO_2$ or $BrONO_2$!) in the initialization until the modeled NO_2 agreed with measured NO_2 at the local time of the SCIAMACHY measurements.

3. Results and Discussion

[16] The zonal mean BrO VMR for the investigated period from 18 to 27 September 2002 together with our estimate of Br_y, calculated from MIPAS CFC-11, are shown in Figures 1 and 2, respectively. In order to test how well the SCIAMACHY BrO measurements agree with our current understanding of the stratospheric bromine chemistry we

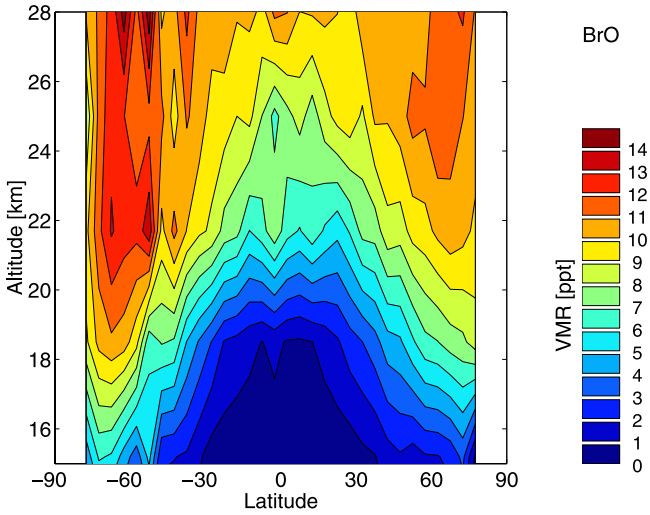

Figure 1. Zonal mean BrO volume mixing ratio measured by SCIAMACHY.

have compared the observed BrO with modeled BrO (Figure 3). The modeled BrO here was calculated by multiplying our Br_y estimate from MIPAS CFC-11 measurements with the BrO/Br_y-ratio from the photochemical model. Two different model runs are shown: (a) a base model run that uses JPL-2002 chemical kinetics and (b) a model run that in addition includes the reaction of $BrONO_2$ + $O(^3P)$ [*Soller et al.*, 2001]. Inclusion of the reaction of $BrONO_2 + O(^3P)$ increases modeled BrO at higher altitudes, but has a negligible effect below about 25 km.

[17] In general we find good agreement between the SCIAMACHY BrO observations and our model calculations assuming 18.16 ppt of total bromine in the stratosphere. The largest differences are seen at low latitudes in the lowermost stratosphere at 18.5 km. Here the SCIAMACHY observations show around 1 ppt while the

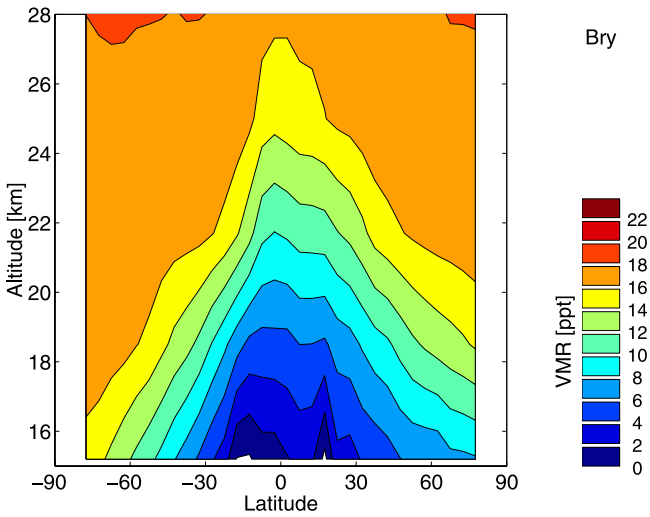

Figure 2. Zonal mean inorganic bromine (Br_y) derived from MIPAS measurements of CFC-11, using the empirical relationship of *Wamsley et al.* [1998]. Note that this estimate of Br_y does also include the contribution of CH_2Br_2 and CH_2BrCl, but not the contribution from $CHBr_3$ or any influx of Br_y from the troposphere.

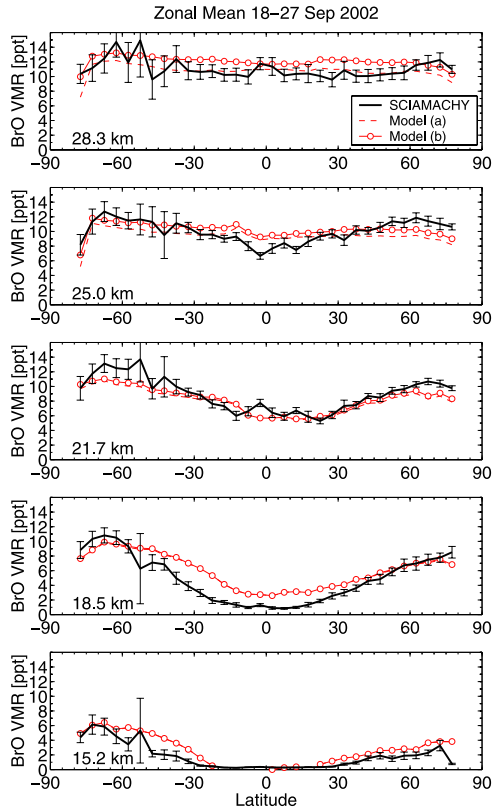

Figure 3. Comparison between BrO VMR from SCIAMACHY measurements and BrO from model calculations for five different altitudes. The modeled BrO was calculated from the product of our estimate of Br_y, which is derived from MIPAS CFC-11 measurements, and the BrO/Br_y ratio from our photochemical model. Model run (a) uses JPL-2002 kinetics, while model run (b) includes in addition the reaction of $BrONO_2$ + $O(^3P)$ [*Soller et al.*, 2001]. Error bars are derived from the standard deviation of BrO measurements within each latitude bin (2 sigma).

expected BrO is at least around 3 ppt. However, we have to await a more comprehensive validation of the BrO and CFC-11 measurements before we can finally decide whether this discrepancy is due to uncertainties in the observations or whether this indicates shortcomings in our understanding of the bromine chemistry in this region.

[18] A comparison between the total BrO vertical column density derived from the SCIAMACHY nadir measurements and the integrated BrO column above 15 km altitude derived from SCIAMACHY limb measurements is shown in Figure 4. The total BrO column from nadir observations with about $3-6 \times 10^{13}$ molecules/cm^2 is similar to previously published total BrO columns derived from GOME observations [*Chance*, 1998]. The integrated BrO column above 15 km is much smaller, implying that there is a significant amount of BrO below 15 km of about $2-4 \times 10^{13}$ molecules/cm^2. Assuming that this BrO background is well mixed between the surface and 15 km, this corresponds to an average tropospheric BrO VMR of about 1.0 ± 0.5 ppt (estimated total uncertainty), with values reaching 2 ppt in the high southern latitudes. Part of the residual column below 15 km altitude will come from BrO in the lowermost stratosphere between the tropopause and 15 km altitude, in

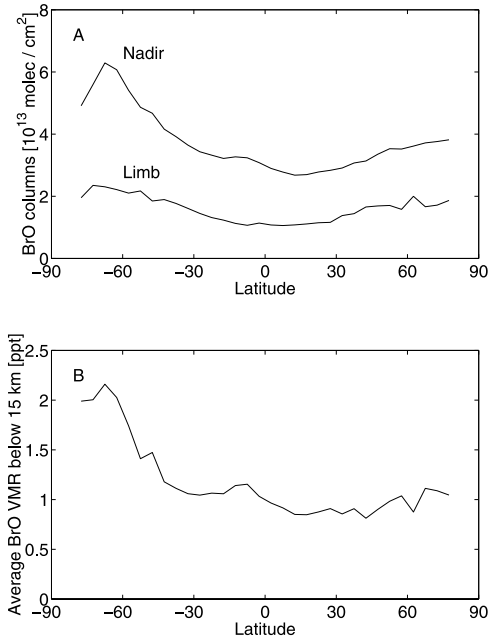

Figure 4. (a) Vertical BrO column above 15 km from SCIAMACHY limb measurements and total BrO column from SCIAMACHY nadir measurements, zonally averaged for the period 18–27 September 2002. (b) Inferred average BrO mixing ratio below 15 km altitude.

particular at high latitudes where this may contribute to the enhanced average BrO VMR seen at high southern latitudes. However, it seems unlikely that a large part of the residual column resides in the lower stratosphere. The tropospheric BrO background of about 1 ppt agrees well with previous estimates from balloon measurements of 0.6–2.0 ppt [*Fitzenberger et al.*, 2000] and is still consistent with the upper limit of 0.9 ppt estimated by *Schofield et al.* [2004]. Observations of enhanced tropospheric BrO columns in high latitude spring have been reported before [*Richter et al.*, 1998; *Wagner and Platt*, 1998] and are attributed to processes on sea ice that release bromine into the atmosphere [*Kaleschke et al.*, 2004].

[19] Taking into account the estimated accuracy of the SCIAMACHY BrO limb retrievals of about 10 to 20%, the observations are overall consistent with a stratospheric bromine loading of 18 ± 3 ppt. This implies a contribution of 3 ± 3 ppt from short-lived source gases in addition to methyl bromide and the halons (Table 1), in agreement with previous studies [*Pfeilsticker et al.*, 2000; *Sinnhuber et al.*, 2002] and the lower end of the range of 4 to 8 ppt given by *Salawitch et al.* [2005].

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