TOTAL AND TROPOSPHERIC BrO derived from GOME and SCIAMACHY as part of the TEMIS project

N. Theys [(1)], I. De Smedt [(1)], M. Van Roozendael [(1)], C. Fayt [(1)], S. Chabrillat[(1)], M. Chipperfield [(2)], P. Post[(3)], R. van der A[(4)]

[(1)] Belgian Institute for Space Aeronomy, Avenue Circulaire 3, B-1180 Brussels, Belgium
[(2)] School of Environment, University of Leeds, Leeds, UK
[(3)] Institute of Environmental Physics, University of Tartu, Estonia
[(4)] Royal Netherlands Meteorological Institute, De Bilt, Netherlands

ABSTRACT

Bromine monoxide plays an important role in the chemistry of the polar atmosphere because of its high efficiency as a catalyst of the ozone destruction in both the stratosphere and the troposphere. In the polar boundary layer, large cyclic emissions are observed every year at spring (the so-called "bromine explosion" phenomenon), which are responsible for the occurrence of fast and efficient tropospheric ozone destruction events. Total columns of BrO have been monitored by the GOME instrument onboard the ESA ERS-2 satellite since 1995. Since July 2002, similar observations can be obtained with SCIAMACHY on the ENVISAT platform. In the present contribution, analyses for total and tropospheric BrO columns derived from both instruments are described, with a focus on the assessment of their mutual consistency. Attempts to extract quantitative estimates of the tropospheric BrO contents over polar and mid-latitude regions are presented, using an algorithm that combines GOME measurements with SLIMCAT 3D chemical transport calculations. Key aspects of the tropospheric BrO retrieval and current sources of uncertainties are discussed.

1. INTRODUCTION

Bromine monoxide (BrO) is a key trace species in the ozone chemistry because of its large efficiency as catalyst of the ozone destruction.

$$Br + O_3 \rightarrow BrO + O_2 \quad (1)$$

$$BrO + O \rightarrow Br + O_2 \quad (2)$$

The action of the BrO in the stratosphere is well characterized although some unresolved issues persist (chemistry and budget) [1]. The bromine trend is dominated by anthropogenic emissions (mainly the halons with a sufficiently long life time to be transported in the stratosphere). Early signs of a trend stabilization have been recently identified [2,3], although these require to be further confirmed. It has long been assumed that reactive halogen species were confined to the stratosphere, playing a significant role only in polar region during spring. However, during the last few years, significant amounts of BrO were also observed in the troposphere first by ground-based instruments [4] and more recently from space by the Global Ozone Monitoring Experiment (GOME) [5,6]. The mechanisms responsible for the production of reactive bromine in the boundary layer and possibly also in the free-troposphere are not well understood. Nevertheless, at the levels produced in the polar boundary layer during the so-called "polar spring bromine explosion events", it is clear that BrO has a strong impact on the tropospheric chemistry, being responsible for complete removal of the ozone within hours or days [4]. Furthermore, the accumulating evidence for the presence of BrO (at levels around 1-3 ppt) in the free-troposphere of polar regions but also at mid-latitude [7], raises the question of the possible impact of reactive halogens on the tropospheric chemistry at the regional scale or even more widespread [8].

Space nadir observations provide BrO columns with global coverage and might help resolving several science issues like:

◊ the estimation of the stratospheric BrO trend to evaluate the impact of Montreal protocol regulations on bromine emissions.

◊ the quantification of the polar BrO emissions and their impact on ozone at the regional scale.

◊ the quantification of free-tropospheric BrO amounts including their latitudinal and seasonal variations and their impact on ozone at the global scale.

However in order to reach these goals, total BrO columns must be resolved into their stratospheric and tropospheric contributions.

This paper describes the algorithmic approach followed at BIRA-IASB to extract total and tropospheric BrO columns from space nadir measurements and their application to GOME and SCIAMACHY. In section 2, important aspects of the tropospheric BrO retrieval are outlined, with particular emphasis on the tropospheric air mass factors and the stratospheric correction. Results obtained with GOME are discussed as to their geophysical consistency and current major sources

of uncertainties. In section 3, BrO column retrievals from SCIAMACHY are presented and their consistency with GOME is investigated. Conclusions and outlook are given in section 4.

2. GOME BrO ANALYSIS

The inversion of BrO slant columns from GOME is performed in the 344.7-359 nm spectral range. The GOME data have been analysed at BIRA-IASB to produce BrO slant columns [9]. So far, approximate vertical columns have been provided using quasi geometric air mass factors (AMF) adequate for a stratospheric absorber. In this paper, we describe attempts to derive tropospheric BrO columns using a combination of GOME and 3D chemical transport model (CTM) data.

The tropospheric algorithm is based on a residual method. The tropospheric contribution is obtained by substracting a stratospheric slant column from the total slant column densities (SCD). The stratospheric BrO correction is derived from estimates of the stratospheric vertical column (VCD) multiplied by an appropriate air mass factor. Finally, tropospheric AMFs, which take into account the surface altitude, ground albedo, cloud fraction and cloud top height, are applied to residual tropospheric SCDs to give tropospheric vertical column densities. The overall structure of the algorithm is outlined on Figure 1.

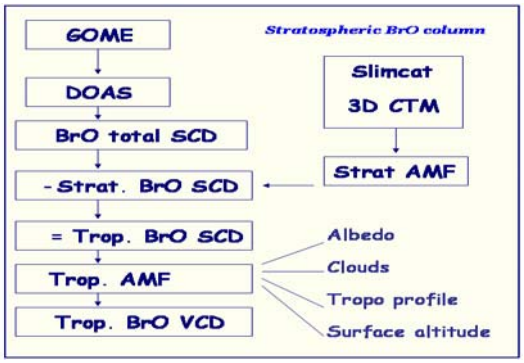

Fig. 1. Overview of the tropospheric BrO retrieval algorithm

A key component is the stratospheric correction. An estimation of the BrO stratospheric background cannot be obtained from GOME in a way similar to that used for NO_2 retrieval [10] because of the difficulty to find an area without any tropospheric contamination. In this work, the approach followed is to use the 3D-CTM SLIMCAT model [11] as a stratospheric BrO reference. The SLIMCAT model contains a detailed chemical scheme and simulates the distribution of all species involved in stratospheric ozone depletion. It has been optimized for bromine chemistry and to some extend validated by comparison with ground –based measurement [12]. Modeled stratospheric BrO profiles are integrated from the tropopause (determined from ECMWF data [13]). An example of the SLIMCAT output is presented in Figure 2.

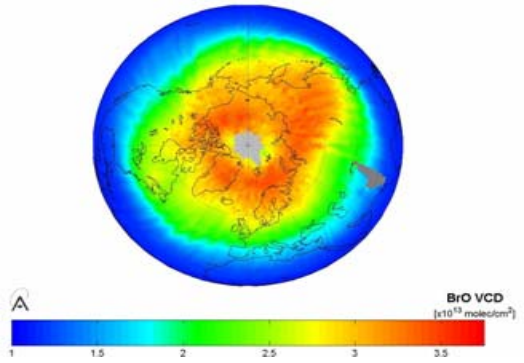

Fig. 2. SLIMCAT stratospheric BrO distribution for March 2001.

2.1. BrO air mass factors

For thin absorbers, the AMF depends on the profile linearly [14]:

$$AMF = \int w(z)\, Prof(z)\, dz \qquad (3)$$

where Prof(z) is the normalized atmospheric profile and w(z) is the so-called weighting function (expressed in cm). The weighting function represents the sensitivity of the measurement at a certain altitude and can be interpreted as a height-resolved AMF. Look-up-tables of BrO weighting functions have been calculated for gridded values of the different parameters.

The influence of ground albedo on the sensitivity of the satellite observations to tropospheric species is strong compared to the stratosphere (Figure 3). The sensitivity to boundary layer is large when the ground albedo is high. The case of high ground albedo is optimal for tropospheric observations since the sensitivity is at maximum and the weighting functions are weakly dependent on the altitude.

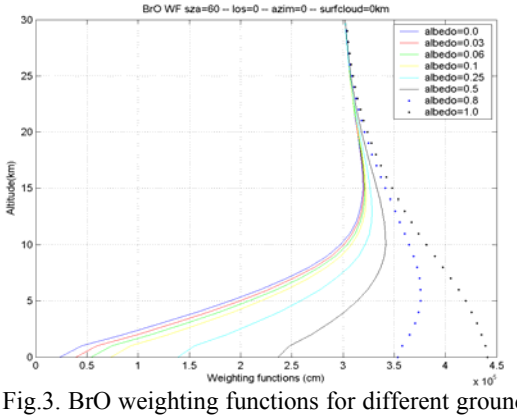

Fig.3. BrO weighting functions for different ground albedo. Calculations are for a solar zenith angle of 60° in a pure nadir viewing geometry.

As the tropospheric AMF is very sensitive to the surface albedo, the monthly database at 335 nm from *Koelemeijer* is used [15].

In first approximation, clouds can be seen as highly reflecting surfaces. If the cloud lies under a BrO layer, BrO measurements are expected to be enhanced by its reflectivity. On the opposite, if the cloud lies above the BrO layer, it will hide BrO from measurements (Figure 4). In principle this effect can be accounted for through the use of a ghost column correction, if it is known.

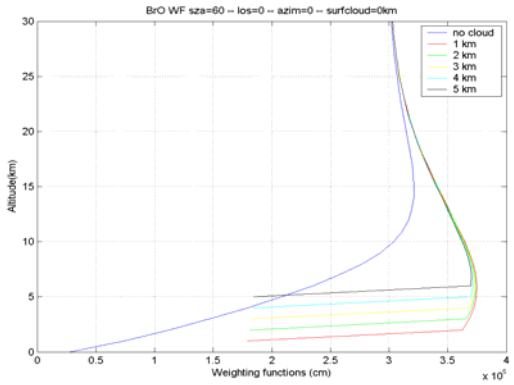

Fig. 4. BrO weighting functions for different cloud altitudes. The curves are associated to completely cloudy scenes at different altitudes.

To account for the effect of the clouds, we use the output of the FRESCO algorithm. FRESCO simultaneously retrieves the effective cloud fraction and cloud top pressure from GOME data [16]. This algorithm makes use of reflectivities as measured by GOME inside and outside the oxygen A band (758-778 nm). Cloud fractions and cloud top pressure from FRESCO are used to weight the AMFs for partly cloudy pixels (independent pixel approximation).

The weighting functions have to be applied to consistent tropospheric BrO profiles (equation 3). Given the current lack of knowledge about the behaviour of BrO content in the troposphere, we have assumed the tropospheric BrO profile to have a free-tropospheric contribution: a gaussian profile with a maximum at 6 km high and a full width half maximum of 2 km has been chosen. This choice is consistent with the only tropospheric BrO profile measurement reported in the literature [17]. A special case has been designed for polar regions with high albedo (snow-ice cover) : if the retrieved tropospheric vertical column exceeds a certain threshold (arbitrary fixed at 6.5e13 molec/cm²) we assume it is because of emissions at the surface level. In this case a different tropospheric profile is introduced: constant in the first 2 km from the altitude of the reflector retrieved by FRESCO. This simulates the "bromine explosion" phenomenon in polar regions in spring. The net effect of this dynamical adjustment of the BrO profile is to increase the size of BrO emissions for polar regions.

Some results of the residual algorithm showing the resulting separation between the stratospheric and the tropospheric part of the BrO columns are presented in Figure 5. The bromine emissions at the surface in polar regions in spring are clearly visible and better isolated from the stratospheric BrO background.

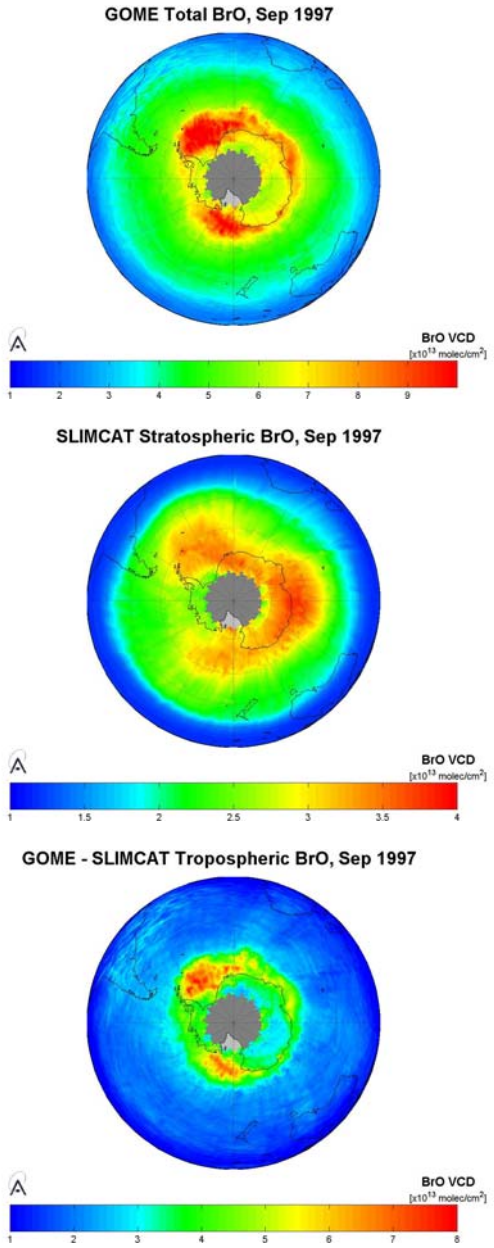

Fig. 5. BrO products for September 1997 in the southern hemisphere. (up) total VCD, (middle) stratospheric VCD, (bottom) tropospheric VCD.

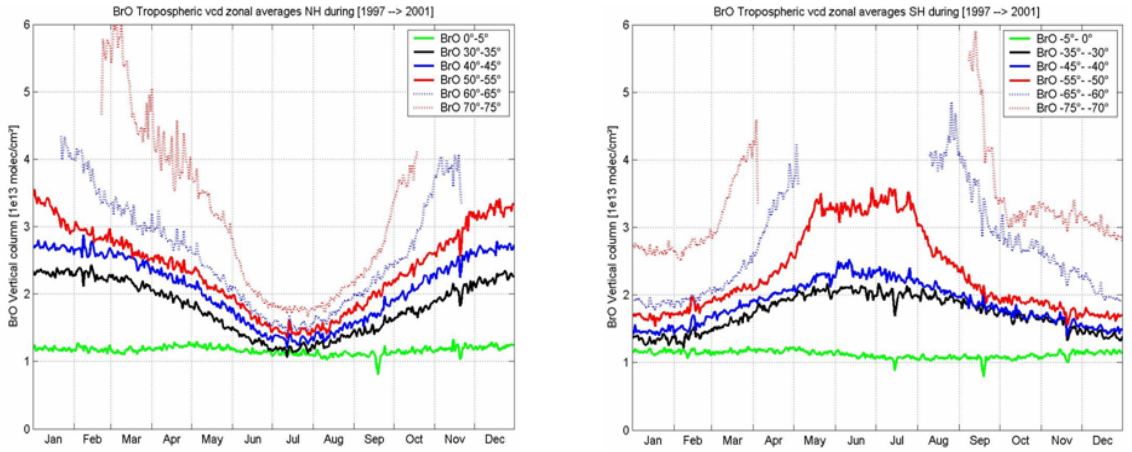

Fig. 6. tropospheric BrO columns time series in northern (left) and southern (right) hemispheres averaged on a 5 year basis (1997 to 2001) for different latitudinal bands.

2.2. Discussion

Using our residual analysis scheme, zonal averages of tropospheric BrO have been computed for all GOME measurements between 1997 and 2001 as displayed in Figure 6. The resulting tropospheric BrO columns show significant seasonal variations and a strong latitudinal dependence in both hemispheres. Large BrO emissions in polar regions in spring are also evidently displayed.

A striking feature of the analysis is, that a non-zero residual tropospheric BrO content is obtained in all conditions whatever the latitude or the season. Stated in other words, this means that BrO columns derived from GOME observations are always larger than simulated by the SLIMCAT model. Since modeled columns are currently not constrained by any observations, the possibility of a systematic underestimation of the stratospheric BrO column by SLIMCAT that would positively bias our tropospheric evaluations can not be ruled out. Such an underestimation of modeled BrO columns could possibly results from the current neglect of several sources of inorganic bromine that may have a significant impact on the budget of the lowermost stratosphere [1]. Additional problems may also arise due to the limited resolution of the model (5° x 7.5°), e.g. :

◊ Fine structures in stratospheric bromine field not well captured by SLIMCAT may result in artifacts especially at high latitude during spring.

◊ The twilight chemistry can be not adequately captured by the model output for regions close to the polar terminator.

Other sources of uncertainties can also be identified and require to be further quantified: BrO slant column density errors, tropospheric AMFs uncertainties (tropospheric profile, surface albedo, cloud correction, snow/ice treatment).

In the present state however, the main issue regarding the accuracy of the tropospheric BrO estimates from GOME is the reliability of the stratospheric correction. In order to investigate the impact of using different model data on the tropospheric algorithm, a preliminary comparison between the BASCOE model [18] (Belgian Assimilation System of Chemical Observations from Envisat, see also bascoe.oma.be) and SLIMCAT has been performed for one GOME orbit, see Figure 7. The BASCOE output is the result from a free run started on the 13 of January 2002 based on initial conditions provided by SLIMCAT.

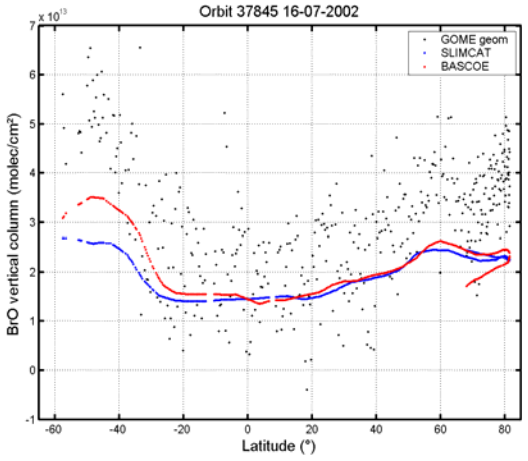

Fig. 7. BrO vertical columns derived from BASCOE and SLIMCAT models for a GOME orbit on 16 July 2002. GOME data are also displayed for comparison.

As can be seen in Figure 7, BrO columns derived from both models are reasonably consistent, which was to be expected since both models use the same assumptions on sources of stratospheric bromine (limited to methyl bromide and some halons coming from the troposphere). However, some significant differences are found in the southern hemisphere (for this particular orbit). More investigations are needed to better understand the origin of these differences and in general to assess the robustness of stratospheric model calculations. Future work will focus on more systematic comparisons between available model and observations of BrO column and profile (ground based and balloon measurements, SCIAMACHY limb profiles). Besides comparison and validation efforts, cloud effects will also be investigated with the aim to identify possible tropospheric signatures (cloud slicing principle).

3. SCIAMACHY BrO ANALYSIS

Observations of BrO total columns have been acquired from space since 1995 by GOME. Since July 2002, SCIAMACHY onboard of ENVISAT has been recording nadir radiance similar to GOME. In principle SCIAMACHY spectra can be processed for BrO using the same tools, however, first attempts to apply the GOME BrO settings to SCIAMACHY rapidly proved to be unsuccessful, mainly due to polarisation features not corrected for in the currently distributed Level-1 data. To overcome these problems, a new UV-shifted fitting interval (336-351.5 nm) was proposed and tested at BIRA-IASB [19].

In the period from July 2002 until June 2003, GOME and SCIAMACHY were operated simultaneously so that the consistency between both instruments could be investigated.
In Figure 8, BrO vertical columns from both instruments are displayed. In both cases, the conversion from slant to vertical columns was obtained using simple stratospheric air mass factors. The good consistency found between both instruments suggests that SCIAMACHY will be able to complete the 8 years coverage of GOME data. In a first effort of independent validation, comparisons between ground-based evaluations and coincident GOME and SCIAMACHY BrO VCDs have been performed in [20]. Both seasonal and short-term fluctuations in the BrO VCDs are captured in the same way by all instruments.

4. CONCLUSIONS AND FUTURE WORK

An algorithm to retrieve tropospheric BrO columns from GOME data has been developed. The tropospheric BrO surface emissions in polar regions are well featured. However significant sources of uncertainties persist in particular as to the determination of the free-tropospheric BrO content at all latitudes. Further investigation will include the assesment of the stratospheric BrO correction quality by making comparisons based on available stratospheric BrO data products (balloon and ground measurements, SCIAMACHY limb profiles, CT Models: BASCOE, SLIMCAT). SCIAMACHY BrO retrievals have been optimized and the resulting columns are found to be consistent with GOME results. The application of the tropospheric algorithm to SCIAMACHY data is therefore also planned. GOME and SCIAMACHY total BrO products are distributed on www.temis.nl.

5. ACKNOWLEDGEMENTS

GOME BrO activities at BIRA-IASB have been supported by ESA/ESRIN, the ESA/OSTC Prodex funding program and the ESA's Data User Program (TEMIS project). The authors wish to thank R. Koelemeijer for FRESCO cloud data.

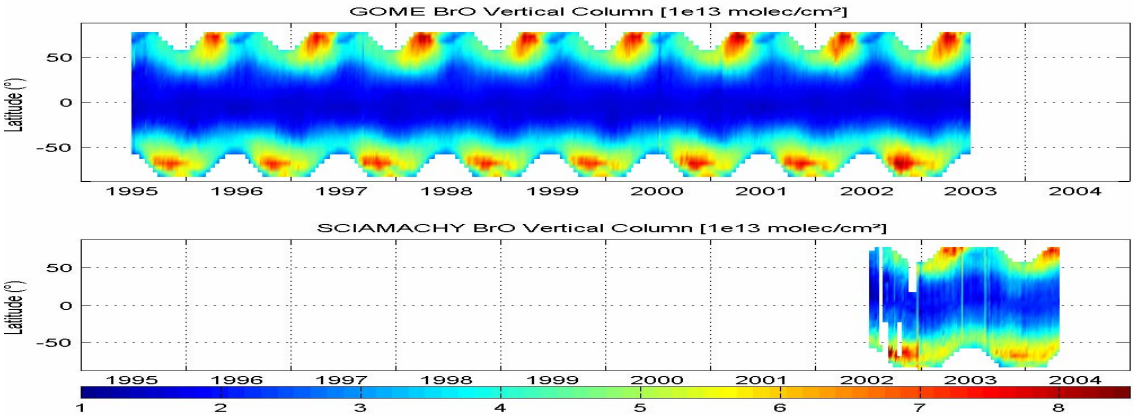

Fig. 8. GOME and SCIAMACHY BrO vertical column distributions.

6. REFERENCES

1. Sioris, C. E., L.J. Kovalenko, C.A. McLinden, R.J. Salawitch, M. Van Roozendael, *Latitudinal and vertical distribution of bromine monoxide and inorganic bromine in the lower stratosphere from SCIAMACHY limb scatter measurements*, J. Geophys. Res., submitted.

2. Van Roozendael, M., F. Hendrick, C. Hermans, C. Fayt and M. De Mazière, *Trend analysis of stratospheric BrO zenith-sky observations at Harestua (60°N) from January 1994 until August 2003*, oral presentation at the SOLVE II / VINTERSOL Joint Science Team meeting, Orlando, Florida, USA, 21-24 October 2003.

3. Montzka, S.A., J.H. Butler, B.D. Hall, D.J. Mondeel, and J.W. Elkins, *A decline in tropospheric organic bromine*, Geophys. Res. Lett., 30(15), 1826,doi:10.1029/ 2003GL017745, 2003.

4. Hausmann, M., and U.Platt, *Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992*, J. Geophys. Res., 99, 25399-25414, 1994.

5. Wagner, T., and U. Platt, *Satellite mapping of enhanced BrO concentrations in the troposphere*, Nature, *395*, 486-490, 1998.

6. Richter, A., F. Wittrock, M. Eisinger, and J.P. Burrows, *GOME observations of tropospheric BrO in northern hemispheric spring and summer 1997*, Geophys. Res. Lett., *25*, pp. 2683-2686, 1998.

7. Platt, U., *Reactive halogen species in the mid-latitude troposphere – Recent discoveries, Water Air Soil Pollut*., 123, 229-244, 2000.

8. von Glasow, R., R. von Kuhlmann, M. G. Lawrence, U. Platt, and P.J. Crutzen*, Impact of reactive bomine chemistry in the troposphere*, Atmos. Chem. Phys. Discuss.,4, 4877-4913, 2004.

9. Van Roozendael, M., C. Fayt, J.-C. Lambert, I. Pundt, T. Wagner, A. Richter, and K. Chance, *Development of a bromine oxide product from GOME*, in Proc. ESAMS'99-European Symposium on Atmospheric Measurements from Space, ESTEC, Noordwijk, The Netherlands, 18-22 January 1999, *ESA WPP-161*, p. 543-547, 1999.

10. Richter, A., and J.P. Burrows, *Tropospheric NO_2 from GOME measurements*, Adv. Space Res., 29, 1673-1683, 2002.

11. Chipperfield, M.P., et al., *Sequential assimilation of stratospheric chemical observations in a three- dimensional model* , J.Geophys. Res., Vol. 107, 4585, 2002.

12. Sinnhuber, B.-M., et al., *Intercomparison of measured and modeled BrO slant column densities*, J.Geophys.Res.,107(D19),4398,doi:10.1029/2001JD000940, 2002.

13. Reichler, T., et al., *Determinig the tropopause height from gridded data* , Geophysical Res. Letters, Vol. 30, No. 20, 2042, 2003.

14. Palmer, P.I., et al., *Air mass factor formulation for spectroscopic measurements from satellites: Application to formaldehyde retrievals from the Global Ozone Monitoring Experiment*, J. Geophys. Res., 106, 14539-14550, 2001.

15. Koelemeijer, R. B. A., *Surface reflectivity spectra derived from GOME data*.

16. Koelemeijer, R. B. A., et al., *A fast method for retrieval of clouds parameters using oxygen A band measurements from the Global Ozone Monitoring Experiment* , J. Geophys. Res., 106, 3475-3490, 2001.

17. Fitzenberg, R., H. Bösch, C. Camy-Peyret, M.P. Chipperfield, H. Harder, *First profile Measurements of tropospheric BrO,* Geophys. Res. Lett., 27, 2921-2924, 2000.

18. Chabrillat, S., D. Fonteyn, M. Van Roozendael and F. Hendrick *Stratospheric chemistry of the Antarctic winter 2002: GOME and MIPAS observations explained by a 3D-PSC-CTM,* SPARC 3rd General Assembly, 2004.

19. De Smedt, I., M. Van Roozendael, T. Jacobs, *Optimization of DOAS settings for BrO fitting from SCIAMACHY nadir spectra*, tech-note, 2004.

20. Van Roozendael, M., et al, *First validation of SCIAMACHY BrO columns*, Proceedings, Atmospheric Chemistry Validation of ENVISAT, ESRIN, 3-7 May 2004