TREND ANALYSIS OF STRATOSPHERIC BrO: COMPARISON BETWEEN SCIAMACHY LIMB AND GROUND-BASED UV-VISIBLE OBSERVATIONS

F. Hendrick(1), A. Rozanov(2), P. V. Johnston(3), O. Puentedura(4), H. Bovensmann(2), M. De Mazière(1), M. Gil(4), K. Kreher(3), B.-M. Sinnhuber(2), N. Theys(1), J. P. Burrows(2), and M. Van Roozendael(1)

(1) *Belgian Institute for Space Aeronomy (IASB-BIRA), Brussels, Belgium, Email: franch@oma.be*
(2) *Institute for Environmental Physics (IUP/IFE), University of Bremen, Bremen, Germany*
(3) *National Institute of Water and Atmospheric Research (NIWA), Omakau, Central Otago, New Zealand*
(4) *Instituto Nacional de Técnica Aeroespacial (INTA), Torrejón de Ardoz, Spain*

ABSTRACT

A trend analysis is performed of stratospheric BrO columns retrieved from SCIAMACHY limb and ground-based UV-visible measurements. We focus on SCIAMACHY limb observations collocated with four NDACC (Network for the Detection of Atmospheric Composition Change) stations where long-term time-series of ground-based UV-visible measurements of stratospheric BrO are available for comparison: Harestua (60°N, 11°E), Observatoire de Haute Provence (44°N, 6°E), Izaňa (28°N, 16°W), and Lauder (45°S, 170°E). At the four stations, a decline in stratospheric BrO is observed in both SCIAMACHY and ground-based UV-vis observations. A good consistency between trend values is obtained at high- and mid-latitudes while SCIAMACHY tends to give a larger decline in the subtropical region. It is concluded from this study that the SCIAMACHY limb BrO profile data set is reliable for trend study of stratospheric bromine.

1. INTRODUCTION

Bromine, together with chlorine, is known to be responsible for the destruction of ozone in the stratosphere through its catalytic reactions with ClO, HO_2, NO_2, and O (e.g., [1]). Bromine monoxide (BrO) is the most abundant inorganic bromine species in the stratosphere during daytime (BrO/Br_y ~0.6 with Br_y = $Br+BrO+BrONO_2+HBr+HOBr+BrCl$). Therefore, BrO is a good quantitative indicator of the total inorganic bromine loading Br_y.

Recently, long-term time-series of ground-based UV-visible and balloon-borne observations of BrO have revealed a decline in the stratospheric bromine loading [2, 3, and M. Dorf, personal communication]. Given the mean age of air in the stratosphere, this trend follows the reported decline of long-lived bromine source gases (methyl bromide (CH_3Br) and halons) observed since mid-1998, as a result of the Montreal Protocol restrictions limiting the production of brominated substances.

So far, no decline in stratospheric bromine has been reported from space-borne observations. Here, the trend of stratospheric BrO is analyzed using SCIAMACHY/ENVISAT limb BrO profiles (version 3.2 of the IUP-Bremen scientific product). SCIAMACHY limb measurements of BrO are particularly suitable for trend analysis mainly because they are most of the time not contaminated by the troposphere, in contrast to nadir observations. This is a significant advantage when studying the trend in the stratosphere of a trace gas species like BrO which is present in both the stratosphere and troposphere. In this work, we focus on SCIAMACHY profiles collocated with four stations belonging to the NDACC (Network for the Detection of Atmospheric Composition Change) network and where long-term times-series of ground-based UV-visible measurements of stratospheric BrO are available for comparison: Harestua in Southern Norway (60°N, 11°E), Observatoire de Haute Provence in Southern France (OHP; 44°N, 6°E), Izaňa in the Northern subtropical region (28°N, 16°W), and Lauder in New Zealand (45°S, 170°E). The periods covered by these observations is 1998-2008 for Harestua, 2005-2008 for OHP, 2004-2007 for Izaňa, and 1995-2005 for Lauder. The SCIAMACHY data set exploited in this study extents from September 2002 to September 2008.

2. SCIAMACHY LIMB BrO OBSERVATIONS

The version 3.2 of the IUP-Bremen SCIAMACHY limb BrO product is used in this study. A detailed description of the retrieval algorithm can be found in [4]. In brief, the retrieval is done in the 338.0-356.2 nm spectral range using the differential two-step inversion approach implemented in the SCIATRAN radiative transfer software package (http://www.iup.uni-bremen.de/sciatran). The ESA Level 1 data of version 6.03 are provided as input to the retrieval algorithm and additional information on pressure and temperature are from ECMWF (European Center for Medium-Range Weather Forecats). The reference tangent height is about 35 km. For the selection of the SCIAMACHY

Proc. 'Atmospheric Science Conference', Barcelona, Spain, 7–11 September 2009 (ESA SP-676, November 2009)

profiles, the following spatial coincidence criterion is chosen: the average latitude and longitude and tangent point should fall within latitude of the stations ± 5° and longitude of the stations ± 10°. This corresponds to a maximum distance between SCIAMACHY and ground-based UV-visible observations of about 750 km. In order to perform a trend comparison study using similar physical quantities for both SCIAMACHY limb and ground-based observations, SCIAMACHY BrO profiles are integrated in the 13-30 km altitude range for Harestua, OHP, and Lauder and in the 15-30 km range for Izaňa.

3. GROUND-BASED BrO OBSERVATIONS

Measured zenith radiance spectra are analyzed using the DOAS (Differential Optical Absorption Spectroscopy) technique [5]. The spectral signatures of BrO, NO_2, O_2, O_4, OClO (only for Harestua), and the Ring effect are taken into account. The retrieval of BrO at the four stations relies on the same Wilmouth et al. [6] BrO cross sections. The fitting windows are the following: 336-359 nm for Harestua, 345-359 nm for OHP, 342-357 nm for Lauder, and 345-356 nm for Izaňa. The DOAS analysis is performed using daily reference spectra. This makes the zenith BrO slant column densities (SCDs) at twilight only sensitive to the stratosphere. One should note that the DOAS analysis for Izaňa is preliminary and has to be consolidated mainly because differences are present in the BrO SCDs when the DOAS analysis is performed by INTA and BIRA-IASB on a selection of spectra. Investigations are currently under progress in order to explain these differences.

As in [2], 80°SZA (solar zenith angle) sunset stratospheric BrO vertical columns are used for the trend analysis. They are derived by integrating low resolution vertical profiles retrieved by applying an optimal estimation profiling technique to sunset (70-94°SZA) zenith BrO SCDs. A detailed description of the profile inversion method can be found in [2, 4]. Sunset BrO SCDs were preferred because they are somewhat less noisy than sunrise ones [2]. Retrieved profiles are not photochemically corrected in order to correspond to the SZA at SCIAMACHY overpass time. This allows to prevent from any impact of such a photochemical correction on the trend values.

4. MODEL FOR TREND ANALYSIS

Since stratospheric BrO shows a marked seasonality with a maximum in winter and a minimum in summer (related to the NO_2 seasonal cycle), a statistical model with a linear trend and seasonal components should be used to fit the SCIAMACHY limb and ground-based UV-visible columns. We have adopted a model described by polyharmonic functions of the form:

$$m(t) = A + B(t - t_0) + \sum_{n=1}^{3} C_n \cos(n2\pi(t - t_0)) + \sum_{n=1}^{3} C_n \sin(n2\pi(t - t_0))$$

where *m(t)* is the monthly BrO column at month t, t_0 is the first month of the period on which the trend model is applied, and *A, B* (linear trend), C_n, and D_n are the fit parameters.

The number of sine and cosine functions is optimized through minimization of the fit residuals. Three sine and cosine functions were found to give the lowest fit residuals.

The standard deviation σ_B of the trend is calculated using the standard deviation σ_N of the remainders of the fit (differences between modelled and observed BrO columns) and their autocorrelation coefficient ϕ:

$$\sigma_B = \frac{\sigma_N}{n^{3/2}} \sqrt{\frac{1+\phi}{1-\phi}}$$

where n is the length of dataset in years.

More information on this statistical model and the method used to determine the significance of the estimated trends can be found in [2].

5. RESULTS

Time series of measured and modeled monthly averaged BrO column abundances over the four stations are presented in Fig. 1. Looking at the common periods where both SCIAMACHY limb and ground-based UV-visible measurements are available (2002-2008 at Harestua; 2002-2005 at Lauder; 2005-2008 at OHP; 2004-2007 at Izaňa), we see that a decline in stratospheric bromine is observed at the four stations for all the different periods. The trend values are statistically significant within the 90% confidence level except for SCIAMACHY over Lauder where a trend of -0.5 ± 0.5%/year is calculated. A good agreement is found between both SCIAMACHY and ground-based observations regarding the trend values except at Izaňa where SCIAMACHY gives a significantly larger decline than ground-based (-3.2 ± 0.5%/year and -1.9 ± 0.9%/year, respectively). This could be an indication of still remaining pointing drift of the SCIAMACHY instrument which is more pronounced in the tropics (SCIAMACHY Quality Working Group (SQWG), personal communication). However, it could also result from insufficient quality of the Izaňa ground-based data set. Thus comparison with consolidated ground-based UV-visible observations at this station (see Section 3) is needed before drawing any conclusion about the origin of this larger decline detected by SCIAMACHY.

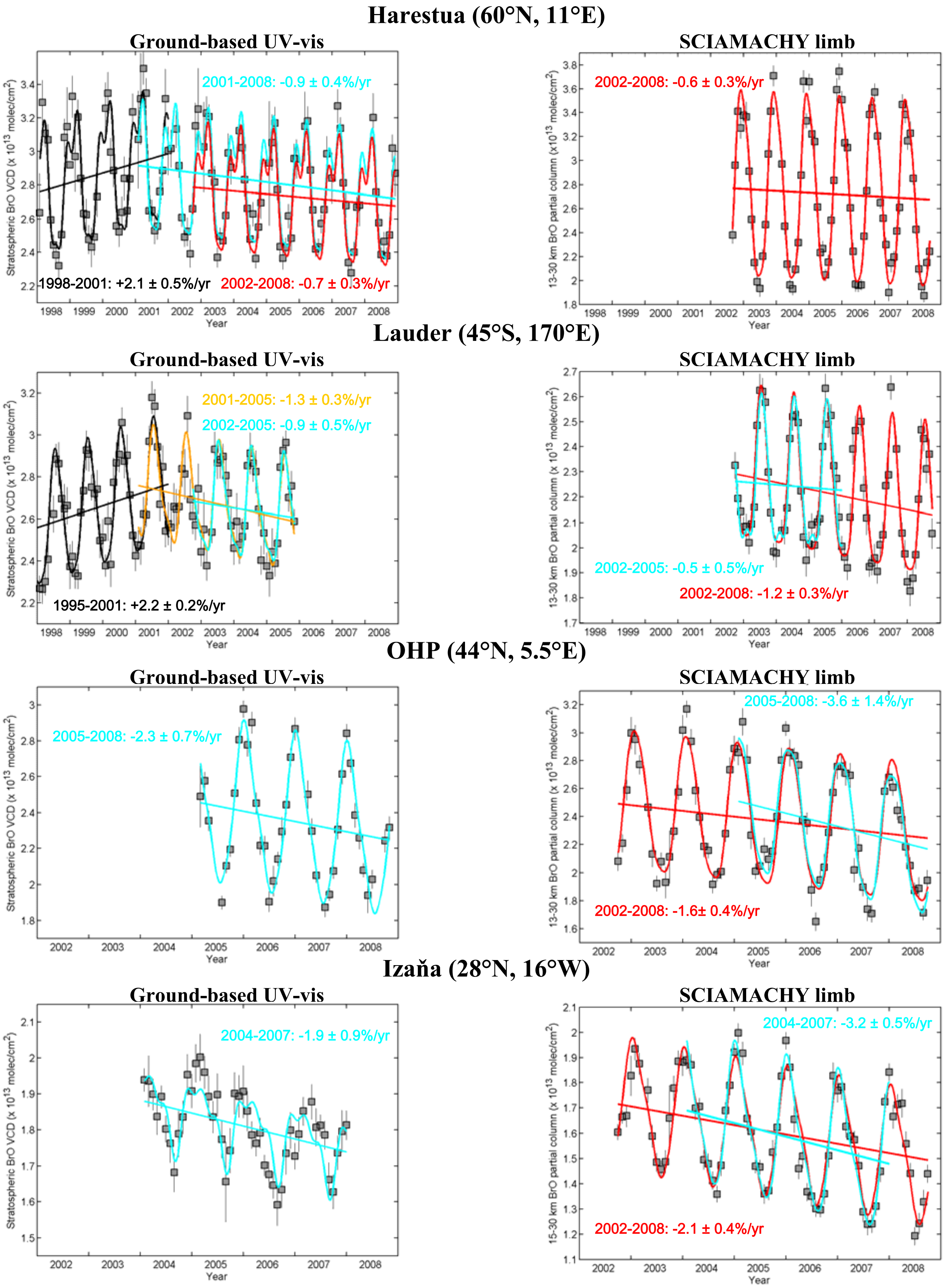

Figure 1: Trend analysis of stratospheric BrO using ground-based UV-vis (left) and SCIAMACHY limb BrO observations (right) over Harestua, Lauder, OHP, and Izaňa.

Stratospheric BrO trend has been also calculated over the 2002-2008 period using the SCIAMACHY limb observations at the four stations and the Harestua ground-based UV-visible data set. This larger time period makes the trend analysis statistically more significant. From Fig. 1, we see that a trend of about -1%/year is found at high- and mid-latitude stations. It is consistent with the estimated decrease of bromine source gases (CH_3Br and halons) observed at the Earth's surface since mid-1998 [7]. At Izaňa, the decline of stratospheric BrO over the 2002-2008 period is about two times larger as compared to other locations but agrees now very well with the results of ground-based observations at this station. Again, further investigations on the significance of this larger decline detected by both SCIAMACHY and ground-based instrument in the subtropical region are needed.

6. CONCLUSIONS

We performed a trend study of stratospheric bromine using SCIAMACHY limb BrO profile observations (version 3.2 of the IUP-Bremen scientific product) over the 2002-2008 period and collocated with four NDACC stations where time-series of ground-based UV-vis measurements of BrO are available: Harestua (60°N), OHP (44°N), Lauder (45°S), and Izaňa (28°N). A decline in BrO columns is observed at the four stations and a good agreement is found between trend values inferred from SCIAMACHY and ground-based UV-visible data sets at high- and mid-latitude stations. These results show that the IUP-Bremen SCIAMACHY limb BrO profile data set is reliable for trend analysis of stratospheric bromine. However, at Izaňa, SCIAMACHY gives a significantly larger decline when using the same time period for both measurements while the trend values are nearly the same if the entire SCIAMACHY data set is used. Further investigations are needed to explain this feature. At high- and mid-latitude stations, the decline over the 2002-2008 period (~-1%/year) is consistent with the decrease of bromine source gases (CH_3Br and halons) observed since 1998. Therefore, after balloon-borne and ground-based UV-visible observations, satellite measurements provide now strong evidences that the Montreal Protocol restrictions on brominated substances have now reached the stratosphere.

7. REFERENCES

1. Lary, D. J. (1996). Gas phase atmospheric bromine photochemistry, *J. Geophys. Res.*, **101** (D1), 1505-1516.
2. Hendrick, F., Johnston, P. V., De Mazière, M., Fayt, C., Hermans, C., Kreher, K., Theys, N., Thomas, A. & Van Roozendael, M. (2008). One-decade trend analysis of stratospheric BrO over Harestua (60°N) and Lauder (45°S) reveals a decline, *Geophys. Res. Lett.*, **35**, L14801, doi:10.1029/2008GL034154.
3. Dorf, M., Butler, J. H., Butz, A., Camy-Peyret, C., Chipperfield, M.P., Kritten, L., Montzka, S. A., Simmes, B., Weidner, F. & Pfeilsticker, K. (2006). Long-term observations of stratospheric bromine reveal slow down in growth, *Geophys. Res. Lett.*, **33**, L24803, doi:10.1029/2006GL027714.
4. Hendrick, F., Rozanov, A., Johnston, P. V., Bovensmann, H., De Mazière, M., Fayt, C., Hermans, C., Kreher, K., Lotz, W., Sinnhuber, B.-M., Theys, N., Thomas, A., Burrows, J. P. & Van Roozendael, M. (2009). Multi-year comparison of stratospheric BrO vertical profiles retrieved from SCIAMACHY limb and ground-based UV-visible measurements, *Atmos. Meas. Tech.*, **1**, 273-285.
5. Platt, U. & Stutz, J. (2008). Differential Optical Absorption Spectroscopy (DOAS), Principles and Applications, ISBN 978-3-540-21193-8, Springer Berlin Heidelberg.
6. Wilmouth, D. M., Hanisco, T. F., Donahue, N. M. & Anderson, J. G. (1999). Fourier transform ultraviolet spectroscopy of the $A(^2\Pi_{3/2}) \leftarrow X(^2\Pi_{3/2})$ transition of BrO, *J. Phys. Chem.*, **103**, 8935-8945.
7. World Meteorological Organization (2007). Scientific assessment of ozone depletion: 2006, Global Ozone Res. and Monit. Proj. Rep. 50, Geneva, Switzerland.

8. ACKNOWLEDGEMENTS

This research was financially supported at IASB-BIRA by the Prodex contract SECPEA and by the EC projects GEOmon and SHIVA (6th and 7th Framework Programs, respectively). IASB-BIRA is also thankful to M. P. Chipperfield for providing the SLIMCAT data needed for the ground-based BrO profile retrieval. The SCIAMACHY limb BrO retrieval activity was partially funded by the German Ministry of Education and Research (BMBF) through the German Aerospace Center (DLR) within the SADOS project (50EE0727). Some data shown here were calculated on German HLRN (High-Performance Computer Center North) and NIC/JUMP (Jülich Multiprocessor System). Services and support are gratefully acknowledged. The IUP Bremen group thanks also the European Centre for Medium-Range Weather Forecats (ECMWF) for providing the pressure, temperature, and surface elevation information (ECMWF Special Project SPDECDIO). NIWA authors thank the New Zealand Foundation for Research Science and Technology for long term support for the Lauder BrO measurements.