Tropospheric and stratospheric BrO and NO_2 columns derived by use of satellite observations and 3D CTM FinROSE

P. Post [(1)], L. Backman [(2)], L. Thölix [(2)], M. van Roozendael[(3)] and C. Fayt[(3)]

(1) University of Tartu, Institute of Environmental Physics, Tartu, Estonia
(2) Finnish Meteorological Institute, Earth Observation, Helsinki, Finland
(3) Belgian Institute for Space Aeronomy, Brussels, Belgium

ABSTRACT

Total slant column densities (SCD) of NO_2 and BrO from the GOME ERS-2 satellite nadir measurements have been split into stratospheric and tropospheric loadings. In order to obtain tropospheric vertical column densities (VCD) two key challenges arise: the quantification of the stratospheric column and the calculation of the tropospheric air mass factor (AMF). Stratospheric NO_2 and BrO columns are derived at the instrument's overpass time by means of a stratospheric chemistry transport model, i.e. FinROSE-ctm, to take into account the stratospheric variability of these trace gases. In order to gain the trace gas tropospheric column the stratospheric slant column is subtracted from the DOAS slant column retrieval.

1 INTRODUCTION

NO_2 and BrO are both photochemically active and their concentrations have a remarkable daily cycle. Furthermore, BrO and NO_2 are present in detectable amounts both in the troposphere and stratosphere. NO_2 plays a key role in both stratospheric and tropospheric chemistry. In the stratosphere NO_2 functions both as an ozone depleting substance and as a terminator in the halogen oxide ozone depleting cycles. While the main sources and source regions in the troposphere are known: thunderstorms and pollution from transportation, power plants and industrial sources, large uncertainties remain on the individual source strengths and their latitudinal and seasonal variations. During daylight the most abundant stratospheric bromine species, which accounts for 60-70% of total inorganic bromine, is BrO [1]. BrO is an important trace species in the ozone chemistry because of its large efficiency as catalyst of the ozone destruction.

Global Ozone Monitoring Experiment (GOME) measurements from the ESA ERS-2 satellite have enabled for the first time to estimate globally the BrO vertical columns in the atmosphere [2, 3]. From GOME measurements also enhanced amounts of BrO in the boundary layer (BL) over the polar regions in spring have been detected [2, 3, 4]. These enhancements have been assigned to the BL because of complete ozone depletion in the BL at the same time. Analysis of ground-based measurements for GOME validation shows that GOME measures more BrO than zenith-sky experiments do [5]. This indicates a global tropospheric background estimated at 1-2 ppt [6].

The mechanisms responsible for the production of reactive bromine in both the boundary layer and in the free-troposphere are not well understood at the moment, although the role of sea-ice and sea-salt aerosol has been clearly identified [7, 8]. Furthermore, the accumulating evidence for the presence of BrO in the free-troposphere of polar regions but also at mid-latitude, raises the question of the possible impact of reactive halogens on the tropospheric chemistry at the regional scale or even more widespread.

The main aim of this study is to develop a relevant methodology for operational retrieval of stratospheric/tropospheric BrO and NO_2 columns. The approach is to estimate the tropospheric columns from the residual of the total columns retrieved by satellite (GOME) and the stratospheric part given by a chemical-transport model.

2 METHODS TO SEPARATE STRATOSPHERIC AND TROPOSPHERIC COLUMNS

From satellite nadir measurements (e.g. GOME, SCHIAMACHY, OMI) the total slant column densities ($\mathbf{SCD_{total}}$) of BrO and NO_2 can be retrieved using DOAS. The residual technique enables to process this total column product and retrieve the tropospheric part of the vertical column density ($\mathbf{VCD_{trop}}$). The difference between total ($\mathbf{SCD_{total}}$) and the stratospheric BrO slant column densities ($\mathbf{SCD_{strat}}$) is attributed to tropospheric BrO. The tracer's tropospheric VCDs are then computed:

$$\mathbf{VCD_{trop} = (SCD_{total} - SCD_{strat})/AMF_{trop}.} \quad (1)$$

The air mass factor – AMF – is the ratio of the slant column density (SCD) of the absorber (i.e. that viewed by the satellite in the measured radiance spectrum) to the vertical column density (VCD):

$$\mathbf{AMF = SCD/VCD.} \quad (2)$$

In Eq. 1 the AMF of troposphere is used.

Investigators have made different assumptions about the stratospheric columns that are based on the observation that stratospheric tracers have a smooth spatial behaviour:

1. In Ref. [9] the Image Processing Technique (IPT) is used to get tropospheric NO_2 columns. Implicit assumption is that over oceanic, cloudy pixels, the retrieved column is in fact the stratospheric column. This is the potential weakness of the method since tropospheric NO_2 may still be present above a cloud.
2. Reference Sector Method [10, 11]. The main tropospheric sources of NO_2 are either anthropogenic or thunderstorms, therefore the total column over a remote Pacific region is assumed as composed of only stratospheric NO_2. The tropospheric loading at any location can then be obtained as the residual of the total column and a latitude dependent stratospheric column of a remote Pacific region. The drawback of the method is that one need to assume longitudinally homogeneous NO_2 and actually a small amount of tropospheric NO_2 may still be present in the reference pixels themselves. However, longitudinal variations can clearly not be neglected close to the Polar Vortex or during major changes in stratospheric dynamics, introducing some artefacts at high latitudes in winter and spring.
3. CTM stratosphere [12, 13]. The stratospheric column of BrO or NO_2 can be obtained from chemistry-transport model (CTM) simulations. The main advantage is that the model accounts for dynamical features in stratospheric NO_2 or BrO, but the drawback is that the retrieval will depend quantitatively on model.
4. Data assimilation [14]. A CTM stratosphere is made consistent with the observations by assimilating the GOME NO_2 data. The advantage of this method over CTM stratosphere is that the dynamical features in stratospheric NO_2 are still predicted by the model, but that the model stratosphere is affected by the actual GOME observations.
5. As the variability of BrO is much lower in the stratosphere than in the troposphere, the short-term variability is ascribed to the troposphere while the annual component is taken as stratospheric variability [15]. The weakness of the method is that tropospheric BrO may have also annual cycle.

The methods 1 and 2 do not suit for BrO because of the ubiquitous BrO tropospheric column. We shall use residual method to separate from total column product stratospheric and tropospheric contributions. The BrO and NO_2 total slant column densities are retrieved from the GOME product of BIRA-IASB and KNMI. The slant column densities for the stratosphere are calculated from the FinROSE-ctm VCD-s multiplying them by stratospheric AMF-s. The tropospheric BrO and NO_2 abundances will be calculated from the difference between measured total and stratospheric SCD-s. Finally, using tropospheric AMF-s the tropospheric SCD-s are converted into VCD-s.

2.1 Uncertainties in retrieval

Derivation of high quality quantitative tropospheric and stratospheric NO_2 and BrO column amounts for individual ground pixels based on the satellite data is a major challenge. The retrieval of tropospheric trace gas species is characterized by large uncertainties, related to clouds, surface albedo, trace gas profile and to the stratospheric column of trace gas and aerosols.

Retrieval uncertainty estimates for vertical tropospheric NO_2 columns based on theoretical error source discussions combined with actual GOME observations have been presented earlier [16]. Regarding the NO_2 error analysis we relay on this study. The retrieval of tropospheric BrO is very similar to retrieval of NO_2: error sources are similar and of the same magnitude.

BrO AMFs have been computed for a number of different scenarios and are used to characterize the dependence of the measurement sensitivity on solar zenith angle, surface albedo, BrO profile and cloud parameters (height, thickness and type). From that analysis we can draw the following conclusions:

1. For stratospheric AMF calculation, we need to vary only the SZA. The ground albedo is assumed the same everywhere (0.05). The BrO AMF variability caused by varying stratospheric profiles has been found to be in the range of 2%, which has very little influence on tropospheric BrO amounts.
2. The BrO AMF has been found to be very sensitive to ground albedo if there are large concentrations of BrO in the lower atmosphere. Therefore the tropospheric AMFs are calculated depending on both SZA and ground albedo. Tropospheric AMFs are also very sensitive to BrO profile. In case of large albedo, BL and free-tropospheric AMFs are similar in size, while BL AMFs are strongly reduced in conditions of low albedo. Simply said, this means that GOME is generally poorly sensitive to surface BrO except above regions of high albedo. As the BrO profile in the troposphere is not well known, the free troposphere profile (maximum concentration of BrO at 5 km) has been used for further calculations, meaning that BL layer BrO contents if present above regions of low albedo will be underestimated (by factor of 2 approximately).

The influence of clouds on AMF can actually be reduced to the albedo effect of clouds. The effect is large for cases of low surface albedo, when instead of low reflector a highly reflecting surface is included below the BrO layer. Then the AMF of the area will be several times larger than before, which brings large differences in BrO VCD-s over all areas except snow and ice regions.

3 DESCRIPTION OF DATA USED IN THE RESIDUAL METHOD

GOME is a 4-channel spectrometer covering the spectral region from 230 to 800 nm with a spectral resolution of 0.2-0.4 nm, with a main objective of global measurement of ozone columns. Other trace gases that have structured absorptions in the visible and UV like NO_2, OClO, SO_2, H_2CO and BrO can also be retrieved from the spectra. There are several GOME products of total columns of NO_2 and BrO, which differ in details. We used the BIRA-IASB GOME product for BrO and KNMI GOME product NO_2 slant columns. For BrO, the analysis is conducted in the 344-360 nm wavelength region where this molecule presents large vibrational structures. The spectral analysis of GOME spectra is performed using WinDOAS, a multi-purpose DOAS analysis software developed over the nineties at BIRA-IASB. More details on the DOAS procedure applied can be found in ref [17]. The retrieval of NO_2 is generally similar to retrieval of BrO. The difference is in the spectral region: the wavelength range 420-450 nm is used.

The BrO air mass factors for the troposphere were very sensitive to the surface albedo; therefore we have used daily UV albedo [18]. There are no large differences in the monthly mean tropospheric BrO VCD-s if to use climatological albedo or daily ones, but the advantage of using daily albedo is seen when taking also clouds into account. FRESCO effective cloud fractions and cloud top pressures from [19] are used to weight the AMF-s for partly cloudy pixels. No attempt is made to account for the presence of snow, ice, or sun-glint. Thus, if cloud-free land or ocean is covered by snow or ice shelves or if a pixel is affected by sun-glint, these areas will show up as having low-altitude clouds with high cloud coverage. The AMF of clouds is taken at the level of effective cloud top pressure. In case of large surface albedo (0.8), the effect of clouds (even to total AMF) is not important. The effect of clouds is actually the effect of highly scattering boundary surface and in case of high boundary layer albedo it is not very important at what altitude this surface is located.

3.1 FinROSE-ctm data

The spatial distribution and the temporal evolution of stratospheric NO_2 and BrO are simulated using the chemical-transport model FinROSE [20]. The FinROSE-ctm is a global 3d grid point model based on the NCAR ROSE model (e.g. [21]). The model covers the relevant gas-phase stratospheric chemical processes. Heterogeneous processes on polar-stratospheric clouds and in sulphate aerosols are also included in the model. In total it accounts for almost 200 reactions, including oxygen, hydrogen, carbon, nitrogen, chlorine and bromine species. The chemical rate constants and cross-sections are taken from refs [22, 23]. Photolysis rates are derived from a look-up table depending on solar zenith angle, ozone column and altitude. The look-up tables have been compiled using the PHODIS-radiative transfer model (e.g. [24]). The chemical rate equations are solved by considering a chemical equilibrium state for short-lived species (e.g. ClO, NO_2, OH, and BrO). A semi-implicit scheme is used for the integration of the more stable reactants (e.g. HNO_3, N_2O). All short-lived species are grouped and integrated using families e.g. $ClOx=Cl+ClO+Cl_2O_2$, $NOx=NO+NO_2$. All long-lived species and families are transported using the semi-Lagrangian flux-form scheme of [25]. ECMWF meteorological data are used as input for simulating the stratospheric chemistry and dynamics.

The output for GOME overpass time (10:30 LT) is available for 37 latitudes, 36 longitudes and 32 levels for the time period from 1996 to 2002. The model output was interpolated onto a vertical grid of 43 log-pressure levels between 0 and 60 km altitude, resulting in a vertical step size of 1.3 km. The tropospheric abundances of chemical species in the model troposphere are given as boundary conditions.

4. VERTICAL COLUMN DENSITIES OF NO_2 AND BRO

The easiest way for model output validation is by looking at the total vertical abundances of species. The chemistry transport model output at 32 levels for FinROSE-ctm (or 18 levels for SLIMCAT) in the atmosphere was integrated over pressure to get the vertical column densities of BrO or NO_2 in molecule/cm^2. As both CTM-s also have some levels in the troposphere the tropopause need to be defined. A limit of 3.5 PVU was chosen to separate tropospheric and stratospheric columns of NO_2 and BrO.

Vertical column densities of NO_2 integrated from CTM output of FinROSE and SLIMCAT in the stratosphere are presented in Fig. 1. Zonal and monthly averaged maps of stratospheric NO_2 VCD-s for 6 successive years beginning with 1996 are shown. The difference in NO_2 monthly zonal mean VCD-s between two model outputs is in average 1·10^{15} molecule/cm^2. The VCD-s from FinROSE-ctm compared to SLIMCAT are generally lower. The annual cycle of NO_2 VCD over the higher latitudes of both hemispheres is similar for two models. But for SLIMCAT the latitudinal zone where the annual cycle is detected is wider: beginning from 30º and going towards poles, compared to 45º- 90º for FinROSE. NO_2 VCD-s of SLIMCAT have nearly the same magnitude of maximum during warm season over both polar regions - 7-8·10^{15} molecule/cm^2. The only zone where FinROSE has higher values is the 10 degrees circle around the North pole.

Zonal and monthly averaged maps of stratospheric and tropospheric BrO VCD-s for 6 successive years beginning with 1996 are presented in Fig. 2. No remarkable interannual variability is expected in stratosphere, as the bromine chemistry is mostly depending on solar radiation variability. For the tropical zone in all years the FinROSE BrO VCD is around 1-1.5·10^{13} molecule/cm^2. For polar summer the values are nearly the same 1.5·10^{13} molecule/cm^2, but for polar and midlatitude winter and spring the values are higher: up to 3.5·10^{13} molecule/cm^2. The first year (1996) results may be affected by model spin-up (the model run was started from 1995). The VCD-s from FinROSE-ctm are generally lower (1-2·10^{13} molecule/cm^2) compared to SLIMCAT (the scale of the colour bars is different for two models). The annual cycle of BrO VCD over the higher latitudes of both hemispheres is shifted: FinROSE gives maximum values of BrO during Dec-Jan for NH and Jun-Jul for SH, while for SLIMCAT the maximum is during late winter, early spring. The amplitude of the seasonal cycle is also lower for FinROSE.

Following from the above, tropospheric BrO VCD-s obtained by the residual technique are overestimated. Especially high values are seen in 1998 and 2000, which also depend on GOME BrO output variability.

5. CONCLUSIONS AND FURTHER STUDIES

Methods to split satellite nadir measured NO_2 and BrO columns to stratospheric and tropospheric parts have been analysed. The main uncertainties for tropospheric column estimation are connected with uncertainties in clouds, surface albedo and a priori profile shape, what affect the tropospheric air mass factor. In certain conditions measured slant columns (cloud covered pixels, with low surface albedo) are not sensitive to tropospheric abundances. It is simple to divide the total column to tropospheric and stratospheric parts with residual technique, but the regions of low tropospheric columns demand stratospheric columns of high accuracy, otherwise the relative errors may exceed hundreds of % and tropospheric columns may become negative. The choice of FinROSE-ctm output for stratospheric columns was a challenge. The stratospheric BrO and NO_2 columns from FinROSE showed similar seasonal and latitudinal variation as the measured (not shown in this article) and SLIMCAT, but the absolute values of FinROSE stratospheric columns were significantly lower. It resulted in to high values for tropospheric columns.

Sussmann [26] has successfully used NO_2 columns measured at high-mountain-site Zugspitze as a pure stratospheric column. But in global scale this approach needs a net of high-mountain-site measurement sites at all latitudes. At the moment the leading technique is the use of chemistry model stratosphere made consistent with the observations by assimilating the measured data. But in this case the assimilation system must consist of stratosphere and also realistic troposphere.

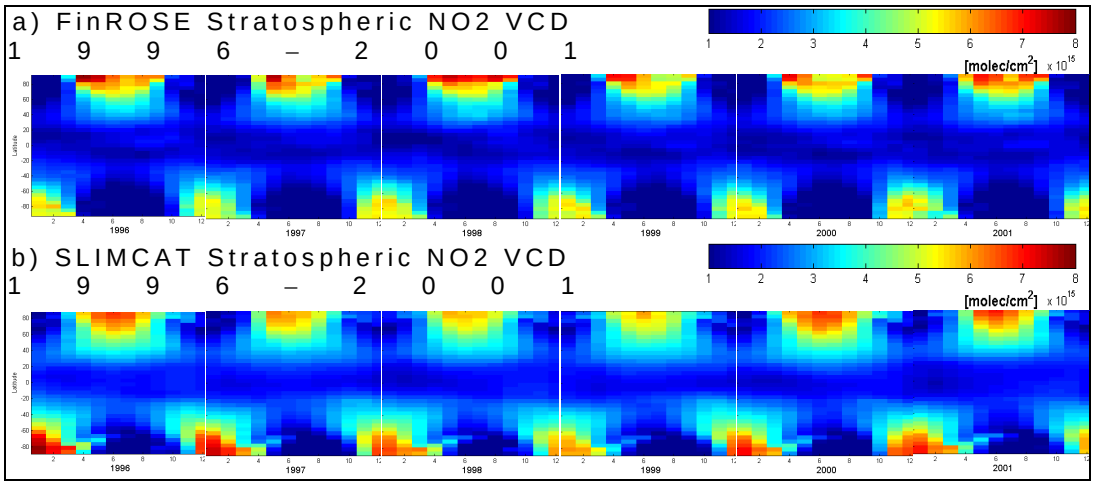

Figure 1. Stratospheric NO_2 VCD-s (in 10^{15} molecule/cm^2) from a) FinROSE and b) SLIMCAT CTM output.

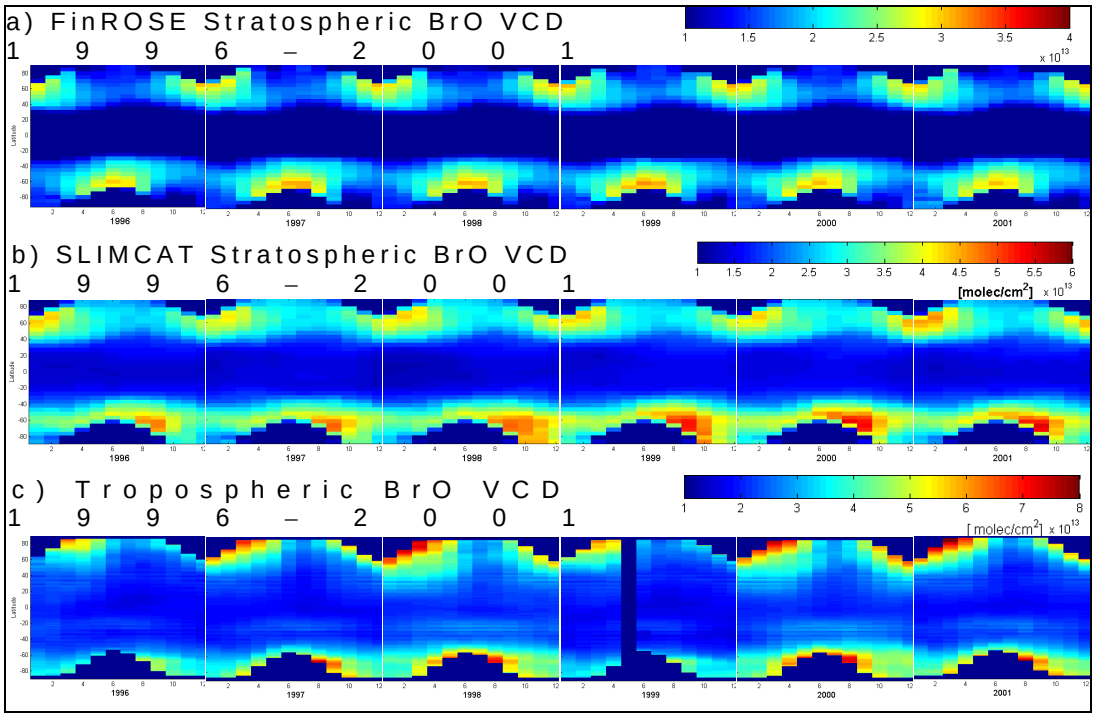

Figure 2. Stratospheric BrO vertical column densities a) from FinROSE-ctm and b) from SLIMCAT output in 10^{13} molecule/cm^2. c) Tropospheric BrO vertical columns calculated by residual method, using FinROSE-ctm data as stratosphere.

Using of stratospheric NO_2 and BrO columns from a stratospheric chemistry transport model offers to take into account the stratospheric variability of these trace gases, but there may be a large bias in model output of trace gases total columns compared to measurements. One possibility to avoid the bias is to scale the resulting model stratosphere NO_2 to "clean" observation conditions by means of a reference sector. This combination of two stratospheric columns retrieval methods gives longitudinal variability to the reference sector method. Usual reference sector method does not suit for BrO because of ubiquitous free tropospheric background. High quality cloudiness data may be useful in this case. From different latitudinal zones reference pixels with optically thick and high clouds are selected. The assumption is that if the pixel is covered with thick and high clouds, signal registered at satellite comes only from the stratospheric BrO. Here can a problem arise from large variability of values of these pixels, this should somehow be resolved. BrO remains a problem also because there are too few measured tropospheric profiles and even stratospheric ones to compile a climatology. SCIAMACHY measured limb and nadir

measurements together offer a complex solution to separate tropospheric and stratospheric columns, but this technique is still in validation phase. The resolution of future instruments will improve, which also require higher spatial resolution from the models.

6 REFERENCES

1. Lary, D.J., Gas phase atmospheric bromine photochemistry, J. Geophys. Res., 101, 1505-1516, 1996.
2. Wagner T. and Platt U., Satellite mapping of enhanced BrO concentrations in the troposphere, Nature, 395, 486-490, 1998
3. Richter, A. et al. GOME observations of tropospheric BrO in Northern Hemispheric spring and summer 1997, Geophys. Res. Lett., No. 25, pp. 2683-2686, 1998.
4. Wagner, T., et al. Spatial and temporal distribution of enhanced boundary layer BrO concentrations measured by the GOME instrument aboard ERS-2, J. Geophys. Res., 106, 225-24,235, 2001.
5. Van Roozendael, M., et al. Intercomparison of BrO measurements from ERS-2 GOME, ground-based and balloon platforms, Adv. Space Res., 29, 1661-1666, 2002.
6. Platt, U. and Hönniger, G., The role of halogen species in the troposphere. Chemosphere, 52, 325-338, 2003.
7. Frieß U., et al. Dynamics and chemistry of tropospheric bromine explosion events in the Antarctic coastal region, J. Geophys. Res., 109, D06305, doi:10.1029/2003JD004133, 2004.
8. Kaleschke, L., et al. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry, Geophys. Res. Lett., 31, L16114, doi:10.1029/2004GL020655, 2004.
9. Leue, C., et al. Quantitative analysis of NOx emissions from GOME satellite image sequences, J. Geophys. Res., 106, 5493-5505, 2001.
10. Richter, A. and Burrows; J.P. Tropospheric NO_2 from GOME measurements, Adv. Space Res., 29, 1673-1683, 2002.
11. Velders, G.J.M., et al. Global tropospheric NO_2 column distributions: Comparing three-dimensional model calculations with GOME measurements. J. Geophys. Res., 106, 12,643-12660, 2001.
12. Van Roozendael, M., et al. Retrieval of Tropospheric BrO and NO_2 from UV-Visible Observations. In Sounding the Troposphere from Space: a new Era for Atmospheric Chemistry. The TROPOSAT Final Report. Peter Borrell, Patricia M. Borrell, John P. Burrows & Ulrich Platt (editors), Springer Verlag, 155-166, 2003.
13. Theys, N., et al. Total and tropospheric BrO derived from GOME and SCIAMACHY as part of the TEMIS project. European Space Agency, (Special Publication) ESA SP (572), pp. 1109-1115, 2005.
14. Eskes H.J. and Boersma, K.F. Averaging kernels for DOAS total-column satellite retrievals, Atmos. Chem. Phys., 3, 1285-1291, 2003.
15. Hollwedel, J., et al. Year-to-year variations of spring time polar tropospheric BrO as seen by GOME. Adv. Sp. Res., 34, 804-808, 2004.
16. Boersma K.F., et al. Error Analysis for Tropospheric NO_2 Retrieval from Space. J. Geophys. Res., 109, D04311, doi:10.1029/2003JD003962, 2004.
17. Van Roozendael, M., et al. Development of a bromine oxide product from GOME, in Proceedings of the European Symposium on Atmospheric Measurements from Space (ESAMS 99), 18 to 22 Jan., ESTEC, Noordwijk, Netherlands, WPP-161, Eur. Space Agency, Noordwijk, Netherlands, pp. 543-547, 1999.
18. Tanskanen, A. et al., Use of the moving time-window technique to determine surface albedo from the TOMS reflectivity data. Proc. SPIE Int. Soc. Opt. Eng., 4896, 239, 2003.
19. Koelemeijer, R. B. et al. A fast method for retrieval of cloud parameters using oxygen A band measurements from the Global Ozone Monitoring Experiment, J. Geophys. Res., 106, 3475-3490, 2001.
20. Damski, J. A chemistry-transport model simulation of the stratospheric ozone for1980-2019. Finnish Meteorological Institute Contributions, 52, 147 pp, 2005.
21. Brasseur, G.P., et al. A three-dimensional simulation of the Antarctic ozone hole: Impact of anthropogenic chlorine on the lower stratosphere and upper troposphere. J. Geophys. Res., 102, 8909-8930, 1997.
22. Sander, S.P., et al. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling Supplement to Evaluation 12: Update of Key Reactions, Evaluation No 13 JPL Publication 00-3, Jet Propulsion Laboratory, Pasadena, CA, 2000.
23. Sander, S.P., et al. Chemical Kinetics and Photochemical Data for use in Atmospheric Studies, Evaluation Number 14, JPL Publication 02-25, Jet Propulsion Laboratory, Pasadena, CA, 2002.
24. Kylling, A., et al. Transmittance of a cloud is wavelength-dependent in the UV-range: Physical interpretation. Geophys. Res. Lett., 24, 397-400, 1997.
25. Lin, S.J. and Rood, R.B., Multidimensional flux-form semi-Lagrangian transport schemes, Mon. Weather Rev., 124, 2046-2070, 1996.
26. Sussmann, R., et al. Stratospheric and tropospheric NO_2 variability on the diurnal and annual scale: a combined retrieval from ENVISAT/SCIAMACHY and solar FTIR at the Permanent Ground-Truthing Facility Zugspitze/Garmisch, Atmos. Chem. Phys., 5, 2657-2677, 2005.

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