

A STRATOSPHERIC BrO CLIMATOLOGY BASED ON THE BASCOE 3D CHEMICAL TRANSPORT MODEL

N. Theys⁽¹⁾, M. Van Roozendael⁽¹⁾, Q. Errera⁽¹⁾, S. Chabrilat⁽¹⁾, F. Daerden⁽¹⁾, F. Hendrick⁽¹⁾,
D. Loyola⁽²⁾, P. Valks⁽²⁾

⁽¹⁾ *Belgian Institute for Space Aeronomy (BIRA-IASB), Avenue Circulaire 3, B-1180 Brussels, Belgium,
E-mail:theys@aeronomie.be*

⁽²⁾ *DLR-IMF, Oberpfaffenhofen, P.O. Box 1116, D-82230 Wessling, Germany*

ABSTRACT

A new climatology of stratospheric BrO profiles has been developed, with the aim to apply it to the retrieval of tropospheric BrO columns from space nadir measurements. The impact of the atmospheric dynamic on the stratospheric BrO distribution is treated by means of Br_y/ozone correlations build from 3D-CTM model results, while photochemical effects are taken into account using stratospheric NO₂ columns as an indicator of the BrO/Br_y ratio. The suitability of the adopted parameterization is evaluated based on one year of output data from the 3D CTM BASCOE. Model simulations include full gas phase chemistry and relevant heterogeneous reactions, while dynamics is driven by ECMWF wind fields.

1. INTRODUCTION

Bromine monoxide (BrO) has been recognized for several years as an important constituent in both stratosphere and troposphere, due to its high efficiency as a catalyst of the ozone destruction. Observations from ground-based [1,2] and satellite nadir platforms [3,4] have shown the spectacular development of highly concentrated BrO plumes produced in the polar boundary layer of both hemispheres in spring. Furthermore, satellite measurements have also suggested the existence of a global free-tropospheric BrO background [3,5,6,7,8,9], with fundamental implications for the chemistry in the troposphere [10]. This last contribution is believed to come from the degradation in the troposphere of the emitted very short-lived (SL) organic bromine substances of natural origin. Moreover, the total stratospheric inorganic bromine burden (Br_y) derived by different observations platforms (balloon [11,12], ground-based [7,9], satellite limb measurements [13,14]) shows a significant higher value than the

transport of the main long-lived organic bromine source gases (methyl bromide and halons) can account for. The emissions of natural SL species in a future warmer climate are largely unknown and might have a significant impact on both stratosphere and troposphere in a long-term perspective [15].

Satellite UV-visible nadir instruments (such as GOME/ERS-2, SCIAMACHY/ENVISAT, OMI/AURA and GOME-2/MetOp-1) offer the unique capability to study and monitor BrO vertical columns (VCD) at the global scale on a consolidated long-term basis. However in order to help solving several science issues related to bromine, the measured total BrO columns must be resolved into their stratospheric and tropospheric contributions. From the measurements alone, there is no way to separate the two components. Further, the approaches used for the retrieval of tropospheric NO₂ columns based on a reference sector method [16] cannot be applied for BrO due to the overall presence of BrO in the global troposphere.

Reference [17] focused on an attempt to extract quantitative estimates of tropospheric BrO content, using an algorithm that combines GOME measurements with SLIMCAT 3D chemical transport model calculations [18]. The possibility of a systematic underestimation of the stratospheric BrO column by SLIMCAT could not be ruled out (this model run was not accounting for the SL species as well as the most recent results [19]). Additional problems may also arise due to the limited resolution of the model.

Here, we report on the development of a stratospheric BrO climatology, based on one year of results of the BASCOE model (see details in section 2). A new approach for the estimation of the stratospheric BrO content is proposed (section 3) with the aim to apply it to the retrieval of tropospheric BrO columns from satellite nadir measurements. Possible

application to historical observations of GOME and SCIAMACHY is also envisaged. The scientific algorithm developed in [17] where a 3D-CTM is used directly for the estimation of a stratospheric correction is a complex approach being not applicable in an operational context. Simplifications have to be found, which will have to be tested. In particular, this method is able to reproduce the important spatial and temporal variations of stratospheric BrO by using dynamical and chemical variables. These variables are directly related to measured quantities, which makes the method simple to implement and guarantee that the results are representative of the sounded pixels. Conclusions and outlook are given in section 4.

2. THE BASCOE MODEL

The Belgian Assimilation System of Chemical Observations from ENVISAT (BASCOE, see bascoe.oma.be) is a 4D-Var assimilation system designed for the analysis and forecast of stratospheric ozone and chemical fields [20,21,22,23]. The model includes 57 chemical species and 4 types of stratospheric PSC particles with a full description of stratospheric chemistry and microphysics of PSCs. All chemical species are advected and interact through 143 gas-phase reactions, 48 photolysis reactions and 9 heterogeneous reactions, all listed in the latest Jet Propulsion Laboratory compilation [24]. PSC microphysics is described by the PSCBox scheme [25] which is coupled to the 3D-CTM core model. The data used in the present study result from a free model run, starting on 1 May 2003 and ending on 30 April 2004. The horizontal resolution is of 1.875° in latitude and 2.5° in longitude. The model is defined on 37 vertical levels, from the surface to 0.1 hPa. It is driven by the ECMWF operational forecasts of winds and temperatures. The model chemical fields are initialized from an output of the SLIMCAT chemical model interpolated to the BASCOE grid. The bromine species are treated in BASCOE by considering a stratospheric inorganic bromine loading of 22 pptv (accounting for 4 pptv from very short-lived species).

3. GENERAL APPROACH

The stratospheric BrO climatology developed here has to meet specific requirements to be

suitable for tropospheric BrO columns retrieval:

- ◇ the climatology has to cover all latitudes
- ◇ the diurnal variation of BrO has to be taken into account, as most of the instruments are sounding the atmosphere for a large range of possible solar zenith angles.

- ◇ stratospheric BrO is highly variable in time and space, and depends on several parameters and atmospheric conditions. The BrO climatology must be able to reproduce accurately the BrO profiles for the large variety of possible scenarios.

BrO in the stratosphere is affected by both the dynamic of the atmosphere and the photochemistry. The bromine monoxide volume mixing ratio profile can be written:

$$BrO = Br_y \times \frac{BrO}{Br_y} \quad (1)$$

where $Br_y = Br + BrO + BrONO_2 + HOBr + HBr + BrCl$ is the inorganic bromine profile accounting for all inorganic bromine species. Br_y can be considered as a good chemical tracer of the dynamic of the atmosphere, due to its long chemical life time. Within a given air parcel transported by stratospheric motion, rapid photochemical reactions between the various inorganic bromine species are taking place, while the initial Br_y volume mixing ratio is an invariant. Thus, Eq. (1) separates the effects on the BrO vertical distribution due to the dynamic of the atmosphere (affecting Br_y) and the photochemistry (affecting BrO/Br_y). In this study, we will treat these two different aspects separately by developing two distinguished “climatologies”. In practice, the key aspect to derive a trustworthy stratospheric BrO profile representative of the measured pixel, is to obtain sufficient information about the dynamical and photochemical state of the sounded atmosphere. As will be shown here, this goal can be reached through the use of a limited number of geophysical parameters.

3.1. Dynamics of the stratosphere

As a first approximation, it can be assumed that air parcels in the lower stratosphere are transported adiabatically. This hypothesis seems plausible for atmospheric motion with typical timescale of ~ 1 day. Several dynamical variables (as potential temperature and potential vorticity) are conserved during adiabatic motions. As Br_y has a very long chemical lifetime and if we assume that the

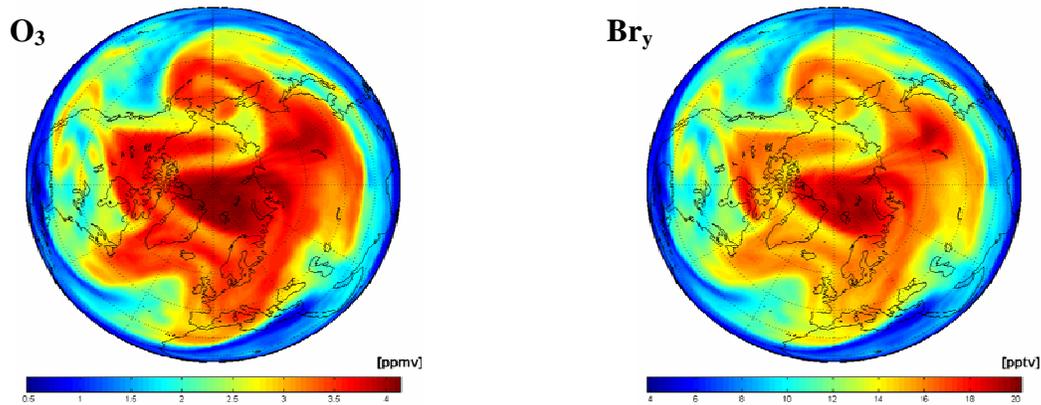


Figure 1. Exemple of BASCOE O_3 and Br_y volume mixing ratios in the northern hemisphere at a potential temperature of $475^\circ K$ (~ 60 mb), for the 1st March 2004 at 00:00 UT.

Sources of Br_y are stable, these variables might be used to evaluate air parcel trajectories and, at the end, to reconstruct reliable Br_y profiles. However, a simpler approach can be adopted which use the O_3 column as a good indicator of the dynamic of the atmosphere. Indeed, it is noticeable that:

◇ Ozone is produced in the stratosphere mainly in the tropical regions and is then transported to mid and high latitudes, by the meridional circulation. For non chlorine activated conditions, ozone in the lower stratosphere can be considered (to a certain point) as a tracer (chemical lifetime ~ 1 month).

◇ Inorganic bromine is mainly produced in the tropical lower stratosphere by the progressive degradation of organic bromine source gases.

Br_y has a very long chemical lifetime and can be transported to higher latitudes.

Since Br_y and O_3 are both produced in the tropical stratosphere and are sensitive to the dynamic of the atmosphere in a similar way, there is a correlation between Br_y and O_3 which can be expected (as illustrated in Fig. 1). Fig. 2 presents the calculated Br_y VCDs as a function of the corresponding O_3 VCDs for the BASCOE data. The scatter plot displays all model values for grid points within a latitudinal band of 10° around $35^\circ S$, for the month of August 2003. There is a quasi correspondence between the ozone column and the Br_y column. The scatter plot will change by varying the latitudinal band and month, illustrating the spatial and seasonal variation of the dynamic of the atmosphere. This noticeable property allows us to build our Br_y profile climatology. Indeed, it is possible to determine a realistic Br_y profile by using a parameterization based only on several inputs: month, latitude and ozone column.

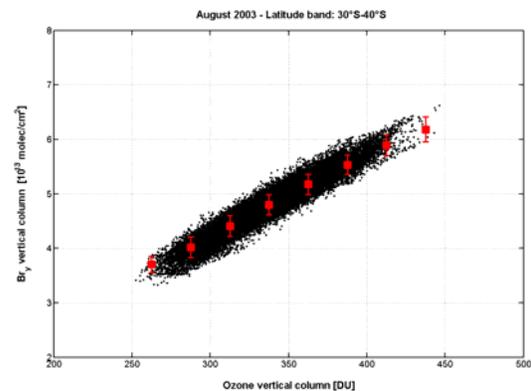


Figure 2. Scatter plot of Br_y and O_3 vertical columns from BASCOE for August 2003 and the latitude band $30^\circ S$ - $40^\circ S$. The red squares correspond to the mean Br_y values for O_3 VCD bins of 25 DU.

In practice, the advantage of this approach is that, besides the simplicity of the method, the ozone column is a standard product which is retrieved operationally with an excellent accuracy and is easily accessible. Furthermore, the retrieved O_3 column is an effective value, representative for the measured pixel. As an example, Fig. 3 presents mean monthly zonal Br_y concentration profiles from the output of the BASCOE model, for March and a latitude band from $40^\circ N$ to $50^\circ N$. The left and right plots correspond to O_3 VCD respectively of 325 ± 12.5 DU and 425 ± 12.5 DU. It has to be noticed that the two profiles are significantly different only below ~ 25 km. For altitudes between the tropopause and 25 km, the Br_y profile is highly variable due to dynamical effects. However, the selection of the Br_y profiles based on the O_3 VCD results in slight deviations from the mean Br_y profiles. It has to be pointed out that this approach fails for ozone-hole

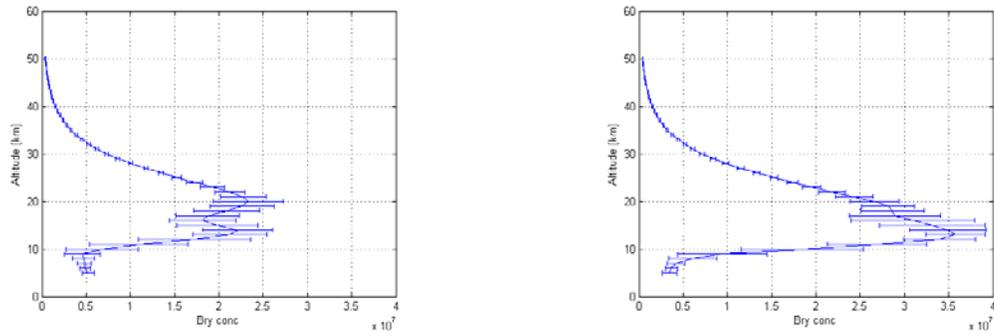


Figure 3. BASCOE Br_y profiles for March and for latitude comprises between $40^\circ N$ and $50^\circ N$ (interpolated on a fixed altitude grid and then averaged level-by-level). The error bars represent the variability of Br_y for each altitude. An additional selection on the model data corresponding to O_3 VCD of (left) 325 ± 12.5 DU and (right) 425 ± 12.5 DU has been applied.

conditions, since ozone can no longer be considered as a dynamical tracer due to its rapid destruction by activated chlorine species. These particular conditions will be further studied in section 3.3.

3.2. Photochemical aspects

In order to determine the partitioning (BrO/Br_y), it is necessary to identify the dominant photochemical reactions as a function of altitude, affecting the bromine partitioning (see discussion in [26,27]). In this section, we restrict ourselves to usual atmospheric conditions. The conditions where the bromine photochemistry is affected by heterogeneous reactions on the surface of PSCs (leading to a denoxification/dehydration of the stratosphere and an eventual activation of chlorine species), is studied in section 3.3. In Fig. 4, the BASCOE volume mixing ratio profiles of the most important bromine species in the stratosphere are plotted for spring mid-latitude typical conditions, during morning daylight (SZA lower than 80°).

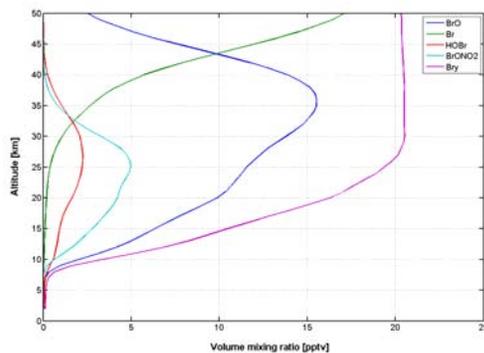


Figure 4. Typical spring mid-latitude volume mixing ratio profiles of BrO , Br , $HOBr$, $BrONO_2$ and Br_y , for morning conditions.

It can be stated that the partitioning of the bromine species in the lower stratosphere depends strongly on the profiles of the reservoir

precursors and on the incoming radiation flux as a function of altitude. The largest contribution to the stratospheric BrO column originates from below 25 km (see Fig. 3). Fig. 4 shows that the main bromine reservoir in this altitude region is $BrONO_2$, which is formed by the termolecular reaction $BrO+NO_2+M$. As a first approximation, the bromine partitioning ratio is given by:

$$\frac{BrO}{Br_y} \approx \frac{BrO}{BrO+BrONO_2} = \frac{1}{1 + \frac{k_{BrONO_2} NO_2}{J_{BrONO_2}}} \quad (2)$$

This relation expresses the balance between the production and the loss (by photodissociation) of $BrONO_2$ which affects directly the bromine partitioning. The key idea for the development of the BrO/Br_y climatology is to use a parameterization based on: (a) the stratospheric NO_2 column (accessible as an intermediate product of the retrieval of total and tropospheric NO_2 columns from satellite nadir observations), (b) the SZA (controlling both diurnal variation of NO_2 and the photodissociation constant).

3.3. Perturbed chemistry conditions

As mentioned earlier, the parameterization of stratospheric BrO based on the O_3 VCD and stratospheric NO_2 VCD is questionable for conditions where the chemistry is altered by heterogeneous reactions on the surface of polar stratospheric clouds (PSC), leading to the effective stratospheric denoxification process and/or the activation of chlorine species. Here, we propose to handle these situations, in our climatology, by adopting a statistical point of view. It has to be pointed out that it is only an approximation of the reality. The mechanisms responsible for the formation of the ozone hole are complex and involve dynamical aspects of the stratosphere and heterogeneous chemistry. Diverse non-linear processes are competing, sometimes with typical timescales varying by

several orders of magnitude. We focus here on the Antarctic region, where the phenomenon is by far more important than for Arctic region, due to weaker dynamic disturbances.

Dynamics of the stratosphere

The discussion in section 3.1, emphasizes the necessity to parameterize the Br_y based on the O_3 VCD (to account for the lower stratosphere dynamical structures) and the latitude and month of the year (to account for the evolution of the meridional circulation of the stratosphere). This approach can be extended, to a certain point, to low O_3 column values (lower than 220 DU). Indeed, in late winter, at the beginning of the ozone hole, the ozone destruction concerns only an upper atmospheric layer where Br_y has relatively smooth spatial and temporal variations (easily reproducible by statistical analysis). So the variations of the O_3 columns within the polar vortex can be related to dynamical patterns also present in the lower stratospheric Br_y field distribution. Later, in spring, the ozone destruction concerns a larger part of the stratosphere (~ 15 to 25 km altitude) and it is no longer possible to identify correlations between O_3 and Br_y in the polar vortex. In this case another tracer of the atmospheric dynamic is needed. Nevertheless, the Br_y vmr shows small variations within the vortex since the air over the polar region is well isolated. In mid-spring, the polar vortex weakens and air masses with low ozone and high Br_y amounts (initially in the vortex) will mix with mid-latitude air rich in ozone and with lower levels of Br_y , leading to an anti-correlation between O_3 and Br_y . It is relatively difficult to represent this mixing in a climatology. In late-spring, the ozone hole has almost disappeared by intense dynamical mixing of air.

Another approach to determine Br_y profiles under ozone-hole conditions would be to use a parameterization using the O_3 profiles retrieved from the measurements. This method seems promising, but is less convenient.

Perturbed photochemistry

The bromine photochemistry deviates from the standard regime (essentially controlled by stratospheric NO_2) under denoxification conditions. Since the denoxification occurs in unpolluted regions, the cases of perturbed bromine photochemistry can thus be diagnosed when low total NO_2 columns are measured (e.g.

lower than $\sim 1 \times 10^{15}$ molec/cm²). Several photochemical scenarios can occur and are illustrated in Fig.5. The temperature and the relative contributions to Br_y from the main inorganic bromine species (BrO, BrCl and HBr) are plotted for an isopotential level ($\theta=440^\circ K$) and for the period from August to mid-October 2003. These values are averaged over the Antarctic polar vortex (NO_x vmr < 0.05 ppbv; morning conditions and SZA lower than 80°).

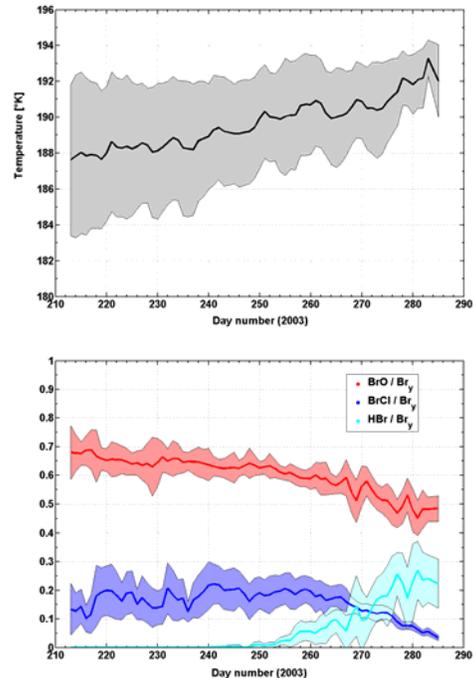


Figure 5. Temperature (top) and partitioning of the main bromine species (bottom) for antarctic denoxification conditions.

We can clearly identify two regimes

◇ denoxification and chlorine activation (~ from August to late September): BrO and BrCl are the major inorganic bromine species. The partitioning BrO/Br_y is relatively stable in time and shows little dispersion.

◇ denoxification and no (or less) chlorine activation (October): As the temperature increases, the PSCs of type 2 evaporate and release HO_x species. Active chlorine is then progressively converted into chlorine reservoirs (mainly HCl). Regarding bromine chemistry, this leads to a photochemical equilibrium mainly between BrO, Br and HBr (BrCl becomes a less important bromine reservoir and HBr is formed by reaction with HO_2). Again, BrO/Br_y shows only small variations.

As a result of the transition between these two particular perturbed photochemical regimes, the

partitioning BrO/Br_y decreases with time. It is also due to the monotonic increase of Br/Br_y during the all period (not shown in Fig. 5), which is a result of the better conversion of BrO into Br as the stratosphere is more exposed to sunlight. From Fig.5, it can be deduced that the temperature of the stratosphere (or a related variable) might be used, to a certain point, as an indicator of the photochemical state of the stratosphere and to determine the bromine partitioning (BrO/Br_y) for denoxification conditions.

4. CONCLUSIONS AND FUTURE WORK

A new stratospheric BrO profiles climatology is being developed, based on dynamical and chemical variables. The parameterization is studied based on output of the 3D CTM BASCOE. The impact of the atmospheric dynamic on the stratospheric BrO distribution is accounted for by using retrieved ozone columns. The effect of photochemistry on stratospheric BrO is determined by considering the stratospheric NO₂ columns. It is also demonstrated that meteorological data as temperature profiles are helpful for the treatment of perturbed photochemical conditions. Before applying this new climatology in the retrieval of tropospheric BrO columns from satellite nadir measurements, further work is still needed in order to:

- ◊ better handle perturbed photochemical conditions during polar spring (including also the arctic region).
- ◊ assess the reliability of the BASCOE reference model results by means of validation using ground-based, balloon and satellite observations.
- ◊ investigate the possible importance of bromine trend effects.

5. ACKNOWLEDGEMENTS

This research has been supported by the Ozone SAF (BrO VS) project and the Belgian Prodex project NOyBry. We wish to thank M.P. Chipperfield (University of Leeds) who provided us with SLIMCAT data.

6. REFERENCES

1. Hausmann, M. and Platt, U., *J. Geophys. Res.*, 99, 25399-25414, 1994.
2. Kreher, K. et al., *Geophys. Res. Lett.*, 24, 3021-3024, 1997.

3. Wagner, T. and Platt, U., *Nature*, 395, 486-490, 1998.
4. Richter, A. et al., *Geophys. Res. Lett.*, 25, 2683-2686, 1998.
5. Van Roozendaal, M. et al., *Adv. Space Res.*, 29, 1661-1666, 2002.
6. Richter, A. et al., *Adv. Space Res.*, 29, 1667-1672, 2002.
7. Schofield, R. et al., *J. Geophys. Res.*, 109, D14304, doi:10.1029/2003JD004463, 2004.
8. Fitzenberg, R. et al., *Geophys. Res. Lett.*, 27, 2921-2924, 2000.
9. Theys, N. et al., Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island, submitted to *Atmos. Chem. Phys. Discuss.*.
10. von Glasow, R. et al., *Atmos. Chem. Phys. Discuss.*, 4, 4877-4913, 2004.
11. Dorf, M. et al., *Atmos. Chem. Phys.*, 6, 2483-2501, 2006.
12. Pundt, I. et al., *J. Geophys. Res.*, 107(D24), 4806, doi:10.1029/2002JD002230, 2002.
13. Sinnhuber, B.-M. et al., *Geophys. Res. Lett.*, 32, L20810, doi : 10.1029/2005GL023839, 2005.
14. Sioris, C. E. et al., *J. Geophys. Res.*, 111, D14301, doi:10.1029/2005JD006479, 2006.
15. Salawitch R.J., *Nature*, 439, 275-277, 2006.
16. Richter, A. and Burrows, J.P., *Adv. Space Res.*, 29, 1673-1683, 2002.
17. Theys, N. et al., Total and tropospheric BrO derived from GOME and SCIAMACHY as part of the TEMIS project, in *Proc. Envisat/ERS Symposium*, Salzburg, 6-10 September, 2004.
18. Chipperfield, M.P. et al., *J. Geophys. Res.*, 107, 4585, 2002.
19. Feng, W. et al., *Atmos. Chem. Phys. Discuss.*, 6, 6695-6722, 2006.
20. Errera, Q. and Fonteyn, D., *J. Geophys. Res.*, 106, 12253-12265, 2001.
21. Daerden, F. et al., *Atmos. Chem. Phys.*, 6, 8511-8552, 2006.
22. Geer, A.J. et al., *Atmos. Chem. Phys.*, 6, 5445-5474, 2006.
23. Vigouroux, C. et al., *Atmos. Chem. Phys.*, 7, 377-396, 2007.
24. Sander, S.P. et al., Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation Number 14, Publication 00-3, JPL, 2003.
25. Larsen, N. Polar Stratospheric Clouds. Microphysical and optical models, Scientific report 00-06, Danish Meteorological Institute, available from <http://www.dmi.dk/>, 2000.
- 26 & 27. Lary, D.J. et al., *J. Geophys. Res.*, 101, 1489-1516, 1996.