Algorithm Document: Retrieval of NO₂ and BrO vertical profiles from SCIAMACHY limb measurements at the University of Bremen

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1 Forward model

Measurements of the scattered solar radiation in limb viewing geometry as performed by the SCIAMACHY instrument are simulated employing the SCIATRAN radiative transfer model [Rozanov, 2004; Rozanov et al., 2005a]. In the spherical mode the model calculates the limb radiance properly considering the single scattered radiance and using an approximation to account for the multiple scattering [Rozanov et al., 2001]. The atmospheric refraction is fully considered whereas the polarization effects are neglected. The SCIATRAN radiative transfer model is linearized with respect to the absorption coefficient, i.e., it can be used to calculate weighting functions of atmospheric trace gases needed by the retrieval procedure to evaluate the vertical distributions.

The weighting function at a particular wavelength, \( \lambda \), is defined as a variation of the outgoing radiance at this wavelength, \( I(\lambda) \), due to a variation in the vertical distribution of the trace gas of interest, \( \alpha \), at a certain altitude level, \( z_i \). For limb measurements the dependence of the outgoing radiance and, therefore, of the weighting functions on the tangent height, \( h_j \), is essential:

\[
W_j(\lambda, z_i) = \frac{\delta I_j(\lambda)}{\delta \alpha(z_i)} \alpha(z_i), \quad j = 1, \ldots, N_{th}, \quad i = 1, \ldots, N_z.
\]

(1)

Here, \( N_{th} \) is the total number of tangent heights and \( N_z \) is the total number of altitude levels.

The radiance and weighting functions simulated with the SCIATRAN model were compared to the results of other radiative transfer models demonstrating a good agreement at viewing geometries specific to SCIAMACHY limb measurements [Loughman et al., 2004; Postylyakov, 2004].

In order to increase the computational efficiency of the radiative transfer model, weighting functions of the atmospheric species are calculated with respect to the single scattered radiance only (so called single scattering weighting functions), i.e.,

\[
W_j(\lambda, z_i) \approx W_{j}^{ss}(\lambda, z_i) = \frac{\delta I_j^{ss}(\lambda)}{\delta \alpha(z_i)} \alpha(z_i), \quad j = 1, \ldots, N_{th}, \quad i = 1, \ldots, N_z.
\]

(2)

where \( \delta I_j^{ss}(\lambda) \) represents the change in the single scattered part of the outgoing radiance due to a change of a trace gas number density at a particular altitude level. The single scattering weighting functions are found to
be sufficient to retrieve vertical profiles of stratospheric species if an iterative retrieval approach is employed, i.e., then the radiative transfer model and the retrieval algorithm are run successively.

2 Retrieval algorithm

The retrieval algorithm consist of two steps, namely, the preprocessing step aimed at getting rid of spectral features not associated to the retrieved parameters and the main inversion procedure.

At the preprocessing step, the ratios of limb spectra at different tangent heights to the measurement at a reference tangent height are treated independently one by one. At each tangent height, a polynomial of an appropriate order is subtracted from the logarithms: (i) of measured limb radiance at this tangent height, $I_j^m(\lambda)$, (ii) of measured limb radiance at the reference tangent height (reference spectrum), $I_{ref}^m(\lambda)$, and (iii) of simulated ratio spectrum, $R_j^s(\lambda)$, (i.e., ratio of modeled limb spectra at current and reference tangent heights, $I_j^m(\lambda)$ and $I_{ref}^m(\lambda)$, respectively) as well as from logarithmic weighting functions in order to account for unknown scattering characteristics of the atmosphere and broadband instrument calibration errors. Resulting functions are denoted as differential spectra, $\tilde{I}_j^m$, $\tilde{I}_{ref}^m$, and $\tilde{R}_j^s$, (measured, reference, and simulated ratio, correspondingly) and differential weighting functions $\tilde{W}_j^k$:

$$\tilde{I}_j^m(\lambda) = \ln[I_j^m(\lambda)] - \sum_{i=0}^{N} a_i^{m,j} \lambda^i,$$

$$\tilde{I}_{ref}^m(\lambda) = \ln[I_{ref}^m(\lambda)] - \sum_{i=0}^{N} a_i^{m,ref} \lambda^i,$$

$$\tilde{R}_j^s(\lambda) = \ln \left[ \frac{I_j^s(\lambda)}{I_{ref}^s(\lambda)} \right] - \sum_{i=0}^{N} a_i^{s,j} \lambda^i,$$

$$\tilde{W}_j^k(\lambda) = \frac{W_k^j(\lambda)}{I_j^m(\lambda)} - \frac{W_k^{ref}(\lambda)}{I_{ref}^m(\lambda)} - \sum_{i=0}^{N} a_i^{k,j} \lambda^i, \quad k = 1, \ldots, N_{tg}.$$

Here, $j$ denotes the tangent height index, $k$ is the retrieval parameter index, $N_{tg}$ is the total number of atmospheric trace gases to be retrieved, and $N$ is a polynomial order. The weighting functions employed here are vertically integrated, i.e., they represent a change of the differential limb radiance due to a scaling of a trace gas vertical profile.

Further in the course of the preprocessing step, a shift and squeeze correction as well as scaling factors for available correction spectra (e.g., ring spectrum, undersampling, stray light correction, etc.) are determined at each tangent height minimizing the following quadratic form:

$$\left\| \tilde{I}_j^m(\lambda) - \tilde{I}_{ref}^m(\lambda) - \tilde{R}_j^s(\lambda) - \sum_k s_k \tilde{W}_j^k(\lambda) - \sum_l c_{l,sc}^i S_l(\lambda) - (c_{shi}^s - c_{sq}^s) \frac{dR_j^s(\lambda)}{d\lambda} - (c_{shi}^{ref} - c_{sq}^{ref}) \frac{dI_{ref}^m(\lambda)}{d\lambda} \right\|^2 \rightarrow \text{min}.$$

Here, $s_k$ are scaling factors for atmospheric trace gas profiles, i.e., $\delta a_k(z_i) = s_k \alpha_k(z_i)$, and $c_{l,sc}^i$ are scaling factors for the correction spectra, $S_l(\lambda)$. Shift and squeeze correction is done for the ratio of the modeled spectra with respect to the measured spectrum, represented by the coefficients $c_{shi}^s$ and $c_{sq}^s$, correspondingly, as well as for
the limb measurement at the reference tangent height with respect to the measurement at current tangent height, represented by $c_{ref}^{sH} \text{ and } c_{sq}^{sH}$. All coefficients here are tangent height dependent, subscript $j$ is omitted for simplicity.

At the inversion step, vertical profiles of atmospheric trace gases are retrieved solving the following equation:

$$ y = K x + \epsilon, \quad (8) $$

where, $\epsilon$ denotes errors of any kind, e.g., measurement noise, linearization error, and so on. The measurement vector, $y$, contains the differences between ratios of simulated and measured differential limb spectra for all spectral points within the selected spectral intervals at all selected tangent heights with all corrections from the preprocessing step, except trace gas profiles scaling, applied, i.e.,

$$ y = [y_1(\lambda_1), \ldots, y_1(\lambda_{Nwl}), \ldots, y_Nth(\lambda_1), \ldots, y_Nth(\lambda_{Nwl})], \quad (9) $$

where $N_{wl}$ is the total number of the spectral points in the selected spectral region and $N_{th}$ is the total number of the selected tangent heights. The state vector, $x$, contains relative differences of trace gas number densities (with respect to initial values) at all altitude layers for all gases to be retrieved, i.e.,

$$ x = [x_1(h_1), \ldots, x_1(h_{Nh}), \ldots, x_Nth(h_1), \ldots, x_Nth(h_{Nh})], \quad (10) $$

where $N_h$ is the total number of layers in the retrieval altitude grid and $N_{tg}$ is the total number of atmospheric trace gases to be retrieved. The linearized forward model operator, $K$, is represented by a matrix having $N_{wl} \times N_{th}$ rows and $N_h \times N_{tg}$ columns containing corresponding differential weighting functions, $\tilde{W}$.

Solution of Eq. 8 is found employing either the optimal estimation method [Rodgers, 2000] or the information operator approach [Hoogen et al., 1999].

The final solution is found iteratively subsequently running the forward model and the retrieval procedure. Since no reliable statistical information on the vertical distribution of NO$_2$ and BrO is available, the Levenberg-Marquardt iteration type [Dennis and Schnabel, 1983; Hanke, 1997] is employed replacing the a priori information at each iteration step by the results obtained at the previous iteration.

3 Auxiliary data

Cross sections:

- NO$_2$: [Bogumil et al., 2003] measured by the SCIAMACHY PFM Satellite Spectrometer at 293, 273, 243, 223, and 203 Kelvin.
- O$_3$: [Bogumil et al., 2003] measured by the SCIAMACHY PFM Satellite Spectrometer at 293, 273, 243, 223, and 203 Kelvin.
- BrO: obtained by the time-resolved Rapid Scan FTS method [Fleischmann et al., 2004] and then convolved to the SCIAMACHY resolution assuming the Gaussian form of the instrument slit function (298, 273, 243, 223, and 203 Kelvin).
- O$_4$: [Greenblatt et al., 1990]

A priori information: climatological data base provided by C.A. McLinden (Personal communications)

Aerosol settings in the forward model:
4 Sensitivity and error analysis

This section is a part of [Rozanov et al., 2005b] paper. All results presented here were obtained employing the optimal estimation method. A priori covariance matrix was represented by a diagonal matrix with diagonal elements corresponding to 100% a priori uncertainty. The measurement error covariance matrix was also diagonal with diagonal elements corresponding to a wavelength independent signal to noise ratio of 2000.

Figure 1 shows the theoretical precision (left plot), averaging kernels (middle plot), and differential weighting functions at 439.4 nm (right plot) for NO$_2$ vertical profile retrieval from SCIAMACHY limb measurements. The results were obtained using the limb measurement at a tangent height of 41.5 km as a reference spectrum. The theoretical precision of the retrieval is about 5% in the altitude region 20–32 km decreasing to 10–20% above 32 km and between 15 and 20 km. Below 15 km the theoretical precision degrades to more than 70% indicating that retrieval results in this altitude region are strongly affected by a priori information. A similar consideration with respect to the information content of SCIAMACHY limb measurements follows then looking at the averaging kernels. Between 18 and 35 km the averaging kernels reach a value of 1.0 at their maxima indicating a complete independence of the retrieved profile from a priori information. Due to a decreasing information content of the measurements and, thus, increasing dependence of the retrieved NO$_2$ amounts on a priori information and on NO$_2$ amounts at the neighboring altitude levels, the averaging kernels become wider and have lower maximum values above and below. For example, looking at the averaging kernel peaking at 12 km one see that the contribution of the true atmospheric state at this altitude to the retrieved NO$_2$ amount is only as high as 45% and the remaining information is originated from upper and lower neighboring altitude levels (by about 15% each) and a priori knowledge. As seen from the right plot in Fig. 1, the weighting functions have pronounced maxima near the tangent height only at tangent heights above 20 km. At lower tangent heights, weighing functions become wider and have a smooth maxima between 20 and 30 km indicating that most of the spectral signal is originating from the higher altitudes rather than from the tangent point region. Nevertheless, down to 12 km tangent heights have different shapes allowing the NO$_2$ amounts below 20 km to be retrieved.

Figure 2 shows the theoretical precision (left plot), averaging kernels (middle plot), and differential weighting functions at 338.6 nm (right plot) for BrO vertical profile retrieval from SCIAMACHY limb measurements. The results were obtained using the limb measurement at a tangent height of 38.5 km as a reference spectrum. Similar to NO$_2$, the theoretical precision of the BrO vertical profile retrieval is about 10–20% in the altitude region 18–28 km decreasing to 20–40% above 28 km and between 14 and 18 km rapidly degrading below 14 km. The peak values of the averaging kernels are close to 1.0 only between 18 and 25 km decreasing to 0.9–0.95 above 25 km and between 14 and 18 km. The peak value of about 0.55 at 12 km altitude indicates an increased dependence of the retrieved BrO amount at this altitude on BrO amount at neighboring altitude levels and a priori information. Looking at the right plot in Fig. 2 one sees that down to 18 km tangent height the weighting functions exhibit relatively sharp peaks near the tangent height, whereas at all tangent heights below 18 km the weighting functions peak at about 18 km altitude. Nevertheless, similar to NO$_2$, the BrO amounts down to 12 km can be retrieved due to different shapes of the corresponding weighting functions.
Figure 1: Theoretical precision (left plot), averaging kernels (middle plot), and differential weighting functions at 439.4 nm (right plot) for NO$_2$ vertical profile retrieval from SCIAMACHY limb measurements.

Figure 2: Theoretical precision (left plot), averaging kernels (middle plot), and differential weighting functions at 338.6 nm (right plot) for BrO vertical profile retrieval from SCIAMACHY limb measurements.
Figure 3: Sensitivity of $\text{NO}_2$ vertical profile retrieval to $a$ priori information. Left plot: true, $a$ priori, and retrieved profiles of $\text{NO}_2$. Right plot: relative deviation of the $\text{NO}_2$ vertical profiles retrieved assuming different $a$ priori profiles with respect to true profile.

Figure 4: Sensitivity of BrO vertical profile retrieval to $a$ priori information. Left plot: true, $a$ priori, and retrieved profiles of BrO. Right plot: relative deviation of the BrO vertical profiles retrieved assuming different $a$ priori profiles with respect to true profile.
Further investigations of the sensitivity of NO$_2$ and BrO vertical profile retrieval were performed using a numerical modeling of the measured data, i.e., a set of limb measurements at different tangent heights was simulated using the forward model assuming a certain state of the atmosphere denoted below as “true”. Thereafter the retrieval was performed considering this set of simulated limb spectra as a real measurement sequence.

Figure 3 shows a set of NO$_2$ vertical profiles retrieved assuming diverse a priori profiles as well as corresponding relative differences between retrieved and true profiles. As clearly seen, the differences are within 10% down to 18 km increasing to 30–40% at 12 km. Thus, in conformance with the conclusions following from theoretical sensitivity investigations above, a substantial influence of a priori information on the retrieved values is observed below 15 km only. Figure 4 illustrates the dependence of the BrO vertical profile retrieval on a priori information in the same manner as Fig. 3 for NO$_2$. Similar to NO$_2$, there is no significant dependence on a priori information down to 15 km.

Figure 5 illustrates the sensitivity of NO$_2$ vertical profile retrieval to the pressure and temperature profiles employed in the forward model. The limb measurement sequence was simulated using the temperature profile marked as “true” then retrieved using in the forward model climatological pressure and temperature profiles appropriate to different latitude regions and NO$_2$ profile appropriate to 65°N (as shown in Fig. 3). The sensitivity of the NO$_2$ vertical profile retrieval to the temperature profile is mainly caused by the temperature dependence of NO$_2$ cross sections employed in the forward model. Above 20 km, retrieved vertical profiles of NO$_2$ are almost independent of the pressure and temperature profiles used in the forward model. At lower altitudes, however, this dependence becomes stronger resulting in relative differences between retrieved and true profiles up to 80%.

Figure 6 illustrates the sensitivity of BrO vertical profile retrieval to the pressure and temperature profiles...
Figure 6: Sensitivity of BrO vertical profile retrieval to the pressure and temperature profiles (climatological profiles in different latitude regions in February). Left plot: temperature profiles used in the forward model. Middle plot: true (gray curve) and retrieved (black curves) profiles of BrO. Right plot: relative deviation of the BrO vertical profiles retrieved using different pressure and temperature profiles with respect to the true profile.

employed in the forward model. Similar to NO$_2$, the limb measurement sequence was simulated using the temperature profile marked as “true” and then retrieved using in the forward model climatological pressure and temperature profiles appropriate to different latitude regions and BrO profile appropriate to 65°N (as shown in Fig. 4). The sensitivity of the BrO vertical profile retrieval to the temperature profile is mainly caused by the temperature dependence of ozone cross sections employed in the forward model. As seen from the plot, the dependence on the pressure and temperature is insignificant between 20 and 30 km increasing to 20–30% above 30 km and between 15 and 20 km. A much stronger influence of the pressure and temperature profiles used in the forward model is observed below 15 km resulting in relative differences between retrieved and true profiles up to 50%.

Thus, the sensitivity region is estimated to be 12–40 km for NO$_2$ and 12–35 km for BrO. Above 15 km, there is no significant dependence of the retrieved profiles on a priori information for both NO$_2$ and BrO, whereas major retrieval problems are expected below associated to the increasing influence of the information originating from the upper and lower neighboring altitude levels as well as from a priori knowledge. The dependence of the retrieved trace gas vertical distributions on the pressure and temperature profiles used in the forward model is insignificant above 20 km, whereas it can not be completely ignored when retrieving the trace gas amounts below.
Figure 7: Comparison of NO$_2$ profiles retrieved from SCIAMACHY limb measurements (v2.1) during January 2005 with the results from SAGE II (v6.2) for different latitude bands. The SAGE II profiles were converted to the solar zenith angle corresponding to the SCIAMACHY measurements using a photochemical model.
Figure 8: Relative deviation between NO$_2$ profiles retrieved from SCIAMACHY ans SAGE II as shown in Fig. 7 for different latitude bands.
5 Product validation

5.1 NO$_2$

Figure 7 shows a comparison of NO$_2$ profiles (v2.1) retrieved from SCIAMACHY limb measurements performed during January 2005 with the results from SAGE II (v6.2) for different latitude bands. The number in brackets at the top of the plots indicate the number of collocations taken into account in the corresponding latitude band. The SAGE II profiles were converted to solar zenith angles corresponding to the SCIAMACHY measurements using a photochemical model. A constant pointing correction of -1 km was applied to SCIAMACHY limb measurements. This is consistent with the pointing correction values retrieved by the TRUE v1.6 algorithm [von Savigny et al., 2005], which uses the vertical profiles of limb radiance in the UV spectral range (around 300 nm) to improve the pointing information (so-called “knee-method”). The relative deviations between SCIAMACHY and SAGE results shown in Fig. 7 are presented in Fig. 8. As seen from the plots the profiles are in a good overall agreement, although SCIAMACHY profiles seem to be vertically shifted with respect to SAGE II profiles. This could be an indication of a still insufficient quality of the pointing correction. Nevertheless, the relative difference between both instruments is mostly within 20% in the relevant altitude range. Results of further validation activities using satellite instruments are presented in [Bracher et al., 2005a,b].

Figure 9 shows a comparison with balloon-born measurements performed by visible DOAS and infrared LPMA spectrometers as well as with the results of SCIAMACHY limb retrievals performed by other groups. Further balloon flights as well as a detailed description of the comparison can be found in [Butz et al., 2005].
Figure 10: Comparison of the BrO profiles (v1.2) retrieved from SCIAMACHY limb measurements to balloon-borne DOAS results. Top left plot: Orbit 5558, Kiruna, March 24, 2003, 09:01 UT. Top right plot: Kiruna, Orbit 10798, March 24, 2004, 10:35 UT. Bottom left plot: Aire sur l’Adour, Orbit 8407, October 09, 2003, 9:51 UT. Bottom right plot: Aire sur l’Adour, Orbit 8421, October 10, 2003, 9:20 UT. The bottom plots show backward and forward matches with the same balloon flight.
5.2 BrO

Figure 10 shows comparisons of the BrO profiles (v1.2) retrieved from SCIAMACHY limb measurements to the profiles obtained with a balloon-borne DOAS instrument, which is a visible spectrometer measuring the transmitted solar light during sunrise, sunset, and balloon ascent. The DOAS profiles were converted to the solar zenith angle appropriate to the collocated SCIAMACHY measurement using a photochemical model. As seen from the plots the profiles are in a good agreement above 20 km. Below 20 km the agreement becomes poor and the retrieval results show a strong scattering. Figure 11 shows comparisons of the BrO profiles (v1.2) retrieved from SCIAMACHY limb measurements to the profiles obtained with a balloon-borne SAOZ instrument, which is a visible spectrometer measuring the scattered solar light during twilight. The SAOZ profiles were converted to the solar zenith angle appropriate to the collocated SCIAMACHY measurement using a photochemical model. As seen from the plots the profiles have the same vertical behavior and agree within the error bars. Although due to large error bars of the SAOZ profiles it is difficult to evaluate the quality of the agreement. Figure 12 shows comparisons of the BrO profiles (v1.2) retrieved from SCIAMACHY limb measurements to the results obtained with the balloon-borne TRIPLE instrument, which performs in situ measurements of BrO employing the chemical-conversion resonance fluorescence technique. For both flights the profiles measured by TRIPLE and SCIAMACHY show the same vertical behavior. For the flight on September 24, 2002 over Aire sur l’Adour the absolute values of BrO volume mixing ratio seen from SCIAMACHY are slightly higher that the mixing ratios detected by the TRIPLE instrument whereas on June 9, 2003 over Kiruna a perfect agreement of the results takes place. Since both instruments measure in the daytime at similar solar zenith angles no photochemical correction is required. The concentration profiles retrieved from the SCIAMACHY measurements were converted using the pressure and temperature profiles measured during the TRIPLE flight. A detailed description of all instruments used in the comparisons can be found in [Dorf et al., 2005].

Comparisons of zonally averaged SCIAMACHY BrO profiles with inorganic bromine (Br\(_y\)) derived from MIPAS
measurements of CFC-11 as well as with modeled zonal means of BrO showing a good qualitative agreement are described by Sinnhuber et al. [2005].

6 Recommendations for product validation

- A photochemical model has to be used to account for diurnal variation of both NO$_2$ and BrO
- NO$_2$ retrievals with version number < 2.0 should only be used above 20 km, only zonally or temporary means can be used below
- BrO retrievals with version number \(\leq 1.2\) should only be used above 20 km, only zonally or temporary means can be used below

References


