Algorithm Document

for the retrieval of OClO, BrO and NO_2 vertical profiles from
SCIAMACHY limb measurements

by

HEIDOSCILI

(Heidelberg DOAS of SCIAMACHY Limb measurements)

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Date: February, 20, 2006

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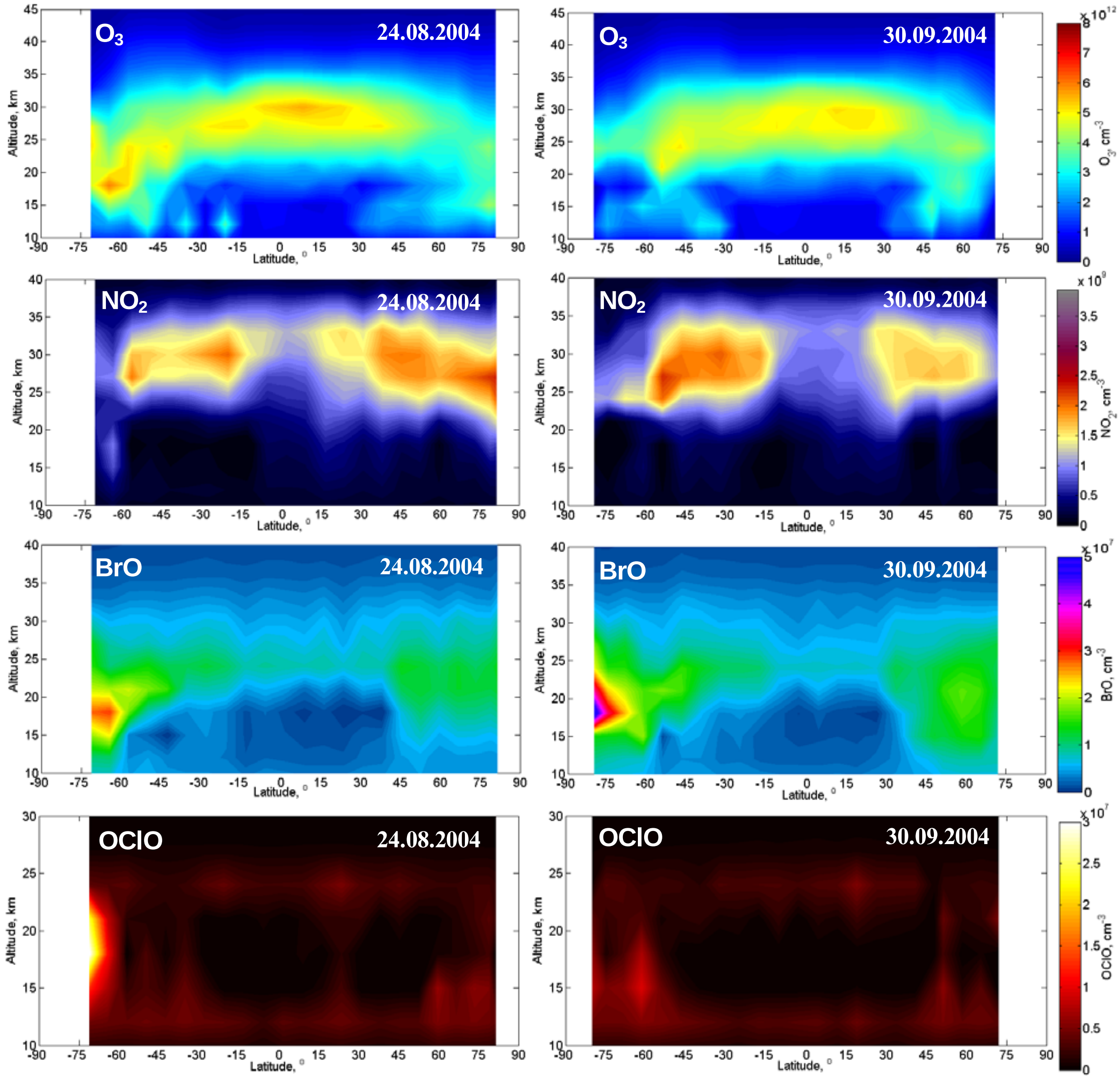

Figure 1: Latitudinal cross sections (concentration as function of altitude and latitude) of ozone, nitrogen dioxide, bromine oxide and chlorine dioxide for selected orbits from 24.08.2004 (right panel) and 30.09.2004 (left panel). Preliminary results. For altitudes from 10 to 15 km the retrieved profile consists mainly of the a-priori information (see Figure 5). Note also that the latitudinal extension of the two orbits differs. Ozone profiles are only retrieved for test purpose and are not a standard product of HEIDOSCILI.

The figure demonstrates very nicely the variety of issues on stratospheric chemistry that can be investigated with the SCIAMACHY limb observations: Substantial depletion of ozone in polar spring (60-70°S), denoxification and denitrification in polar winter, bromine monoxide showing only little dependence on season (compared to OClO), and activation of chlorine in winter and deactivation in spring.

Retrieval algorithm

For the retrieval of vertical profiles (OClO, BrO and NO_2) from the SCIAMACHY limb measurements, we apply a two step approach: First, slant column densities (SCDs) of the respective atmospheric absorbers are retrieved by Differential Optical Absorption Spectroscopy (DOAS). In the second step, box air mass factors calculated by the Monte Carlo radiative transfer model "TRACY" are applied as weighting functions to convert the SCDs (as function of tangent height) to vertical concentration profiles (number densities as function of altitude). The inversion is stabilized by an optimal estimation method based on Rodgers (2000). For the resulting profile, the error of the retrieved SCDs and the variability of the a priori climatology are taken into account. The resulting averaging kernels determine the altitude range where the measurement provided information on the profile: Larger values indicate a large impact of the measurement, for lower values of the averaging kernel the retrieved profile approaches the a priori information.

Forward model

Based on the Lambert Beer law, optical densities of the respective trace gas absorptions are determined. Therefore, the spectral absorption of the considered absorbers i.e. their absorption cross sections need to be known. The key concept of DOAS is to utilize not the absolute absorption structures but to separate them in a broadband and a differential cross section (Platt, 1994; Platt and Stutz, 2005). This enables the detection also of weak absorbers like e.g. BrO and OClO. As results, SCDs - the integrated concentration of the absorber along the light path - are obtained (the optical density of an absorber is the product of its absorption cross section and it's SCD).

In the retrieval algorithm, the difference of the Fraunhofer reference spectra (containing no absorption of the considered trace gas) to the measured spectra is minimized by weighting the absorption cross sections σ_j with the respective SCDs S_j. Broadband absorption and scattering is modelled by a polynomial of degree 3-5. The difference between the logarithm of the reference spectra $I(\lambda)$ on one side and the logarithm of $I_0(\lambda)$ and the sum of the trace gas absorptions and the broadband polynomial on the other side is by applying a least square fit over all wavelengths λ:

$$\ln I(\lambda) - (\ln I_0(\lambda)) - \sum_j S_j \sigma_j \ - \sum_p a_p \lambda^p) \rightarrow 0 \qquad [1]$$

Radiative transfer is simulated by the full spherical Monte Carlo RTM "TRACY" (von Friedeburg, 2003). Applying the viewing geometry of the SCIAMACHY instrument, box air mass factors are calculated that describe the impact of atmospheric layers at all considered altitudes on the SCD measured at a certain tangent height.

With the calculated box AMFs A_{ij} the impact of trace gas concentration (x_j) at different layers of atmosphere to measured SCDs (y_i) can be written:

$$\begin{pmatrix} y_1 \\ y_2 \\ \dots \\ y_m \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{11} & \dots & A_{2n} \\ \dots & \dots & \dots & \dots \\ A_{m1} & \dots & \dots & A_{mn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \dots \\ x_n \end{pmatrix} + \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \dots \\ \varepsilon_n \end{pmatrix} \qquad [2]$$

To retrieve the trace gas concentration profile **x** equation [2] should be inverted. Since the problem is not exact (SCDs have error $\boldsymbol{\varepsilon}$ and corresponding error covariance S_ε) and underdetermined, a-priori knowledge x_a and its covariance S_a are used to exclude unrealistic solutions.

Therefore, the inversion is constrained by a priori knowledge (e.g. a climatology profile) using a linear optimal estimation (maximum a posteriori) method based on *Rodgers* (2000):

$$\mathbf{x} = \mathbf{x_a} + S_a A^T [A S_a K^T + S_y]^{-1} (\mathbf{y} - K\mathbf{x_a}) \qquad [3]$$

Figure 2 summarizes the retrieval steps and information considered for the determination of vertical profiles from the spectra measured by SCIAMACHY.

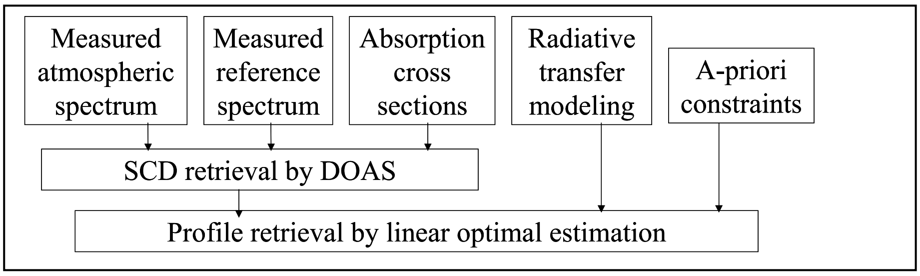

Figure 2: Diagram of the HEIDOSCILI algorithm.

Inversion procedure

For the DOAS analysis, different wavelength ranges are utilized that have been found optimal for the respective trace gas (see e.g. Wagner, 1999 and Wagner et al., 2001): For OClO the fit-window ranges from 363-391 nm, for BrO from 337-357 nm, and for NO_2 from 430-450 nm. Figure 3 shows examples of DOAS analysis for OClO and BrO.

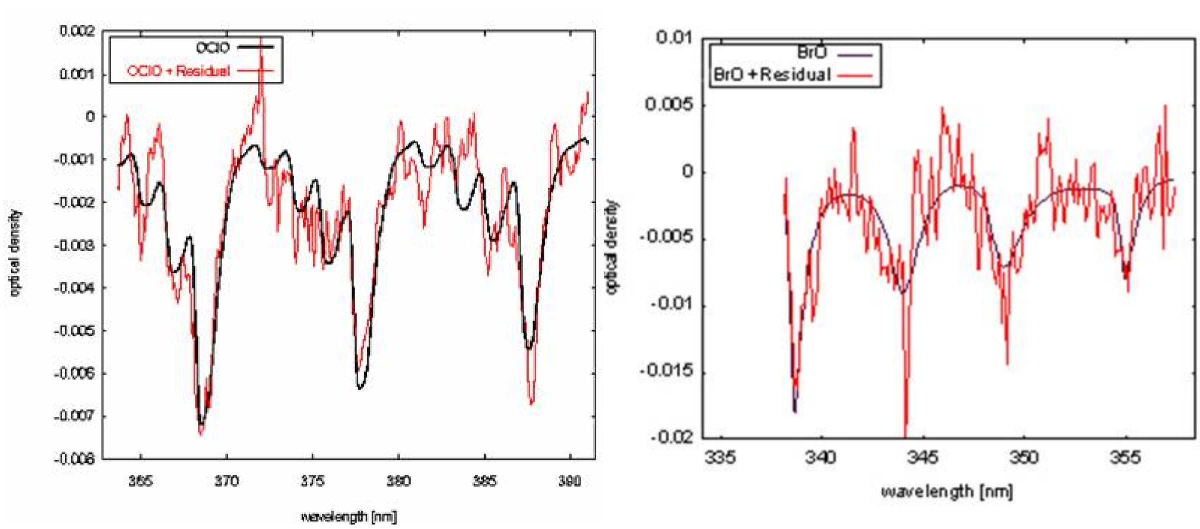

Figure 3: Example for an analysis of SCIAMACHY limb spectra for OClO (right panel) and for BrO (left panel).

As reference the tangent height of 36 km is applied, where both OClO and BrO absorption can be regarded as negligible. For the NO_2 retrieval the reference spectrum is taken at a tangent height of 40 km.

In this first step of the retrieval, SCDs as function of tangent height are obtained. The full inversion is then performed by applying the modelled box AMF to the measured SCDs according to equation [2].

Figure 4 shows an example for a calculation of box air mass factors.

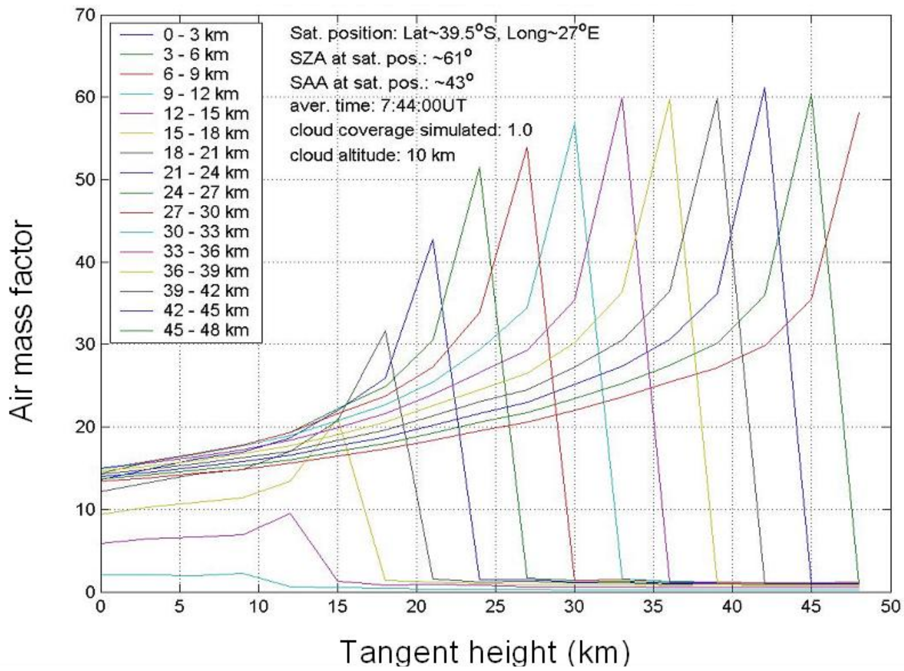

Figure 4: Air mass factors for 3 km boxes with constant concentration, as modelled with the RTM TRACY (von Friedeburg., 2003). The air mass factor (AMF) describes the sensitivity of a given observation with respect to the atmospheric vertical column density (VCD). The accurate values of the AMFs depend critically on wavelength, aerosol profile, solar zenith angle and further quantities.

Further information on the retrieval can be found in Kühl (2005) and Pukite et al. (2005).

Auxiliary data

Absorption Cross sections applied:
O_3: Bogumil et al. (2000), Proceedings of the ERS-Envisat-Symposium, Goteborg, Sweden.
OClO: Krominga et al. (2003), *J. Photochem. Photobiol. A.*: *Chemistry,* 157, 149-160.
BrO: Wilmouth et al. (1999), *Phys. Chem., 103,* 8935-8944.
NO_2: Vandaele et al. (1998), *J. Quant. Spectrosc. Radiat. Transfer*, 59, 171-184, 1998.
Ring-Spectrum: calculated (Bussemer, 1993)

A priori information for the inversion is taken from various sources.
For NO_2, the climatology by Anderson et al. (1986) is applied, scaling the profile to the SZA of the measurement by photochemical modelling.
For BrO, profiles based on balloon measurements (Fitzenberger, 2000; Dorf (2005)) are calculated for the corresponding SZA.
For OClO, a modelled profile calculated for the respective SZA is taken as a priori.

Sensitivity and error analysis

For determining the sensitivity of the measurement at the different altitudes, i.e. the impact of the observations on the retrieved profile, it is essential to consider the averaging kernel of the retrieval. Figure 5 shows typical averaging kernels of the two step approach utilized in HEIDOSCILI.

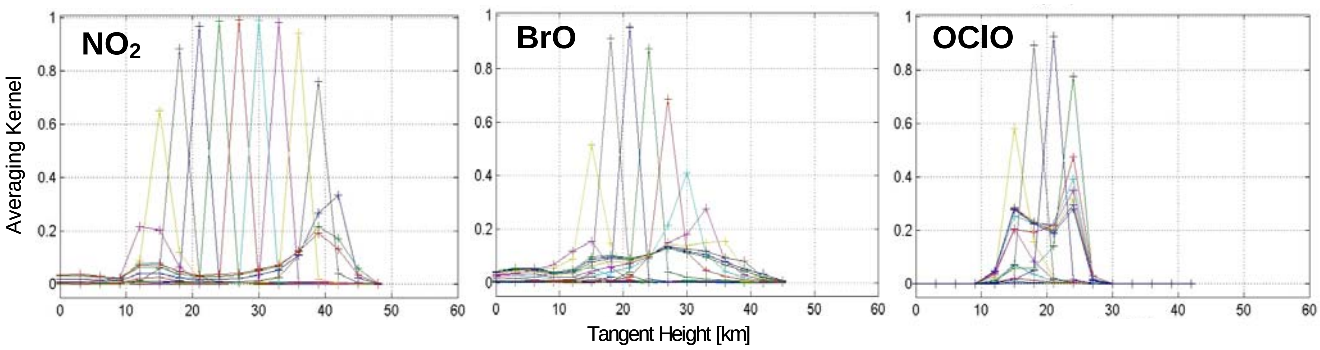

Figure 5: Averaging kernels for typical retrievals of NO_2 (left panel), BrO (middle) and OClO (right) vertical profiles from the SCIAMACHY limb observations.

They reveal that information about the vertical profile can be obtained for NO_2 in the altitude range from 15-40 km, for BrO from 15-28 km and for OClO from 15-25 km. Note that the retrieved profile is practically independent of the a priori for these altitudes. The vertical resolution of the retrieved profile in this altitude range is approx. 3 km. In this range, the error for the OClO profile is estimated to be 50–100%, for the BrO profile, the error is estimated to be 20–100% and for the NO_2 profile, the error is estimated to be 10-50%.

Algorithm validation

The results have been tested for reasonability and compared to SCIAMACHY limb retrievals from other institutes.
For NO_2, a few profiles have been compared to balloon measurements (Butz et al., 2005). Also for BrO, comparisons to balloon measurements (Dorf, 2005) have been formed and it was found that the profiles show a good agreement.
For OClO, the retrieved values for the number density are in good accord with modelled values and balloon measurements, and the height of the profile maximum agrees with expectations.

Recommendations for product validation

Profiles should only be considered as SCIAMACHY measurements for these altitudes where the averaging kernel is large (see Figure 5).
For all species the dependence of the observed concentrations on the SZA needs to be considered. This is valid for NO_2 but even more for BrO and OClO, especially at large SZAs. Thus a photochemical model should be applied when comparing to independent observations.

References:

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List of abbreviations

AMF	Air mass factor
RTM	Radiative Transfer Modelling
SCD	Slant Column Density
SZA	Solar zenith angle