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# Multi-year comparison of stratospheric BrO vertical profiles retrieved from SCIAMACHY limb and ground-based UV-visible measurements

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## Abstract

Vertical profiles of stratospheric bromine monoxide (BrO) daily retrieved from ENVISAT/SCIAMACHY (ENVIronmental SATellite/SCanning Imaging Absorption spectrometer for Atmospheric CHartographY) limb scatter data and from ground-based UV-visible observations performed at Harestua (60° N, 11° E), Observatoire de Haute-Provence (44° N, 5.5° E), and Lauder (45° S, 170° E) are compared in the 15–27 km altitude range for the period from 2002 until 2006. At the three stations, the SCIAMACHY and ground-based UV-visible profiles agree reasonably well, with relative difference smaller than 23% on average. When comparing the BrO partial columns, the agreement obtained is good, with mean relative differences smaller than 11% and corresponding standard deviations in the 13–19% range. The seasonal variation of the BrO columns at the three stations is consistently captured by both retrievals as well as large BrO column events occurring during the winter and early spring at Harestua which are associated with chlorine activation.

## 1 Introduction

Owing to their global spatial and temporal coverage, space-borne sensors are a key component of the global atmosphere observing system, playing a crucial role for understanding and monitoring climate change and ozone depletion. The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) is one of these sensors. It has been launched in March 2002 on board the European ENVIronmental SATellite (ENVISAT). In the nadir and limb viewing geometries, the SCIAMACHY instrument measures the sunlight scattered by the Earth's atmosphere or reflected by the surface whereas in the occultation mode, the direct solar or lunar light transmitted through the atmosphere is observed. The measurements are performed in eight spectral channels covering the 240–2400 nm wavelength range. A detailed description of the SCIAMACHY instrument, its observation modes as well as mission objectives and



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target atmospheric species is given by Bovensmann et al. (1999). Most well-studied and widely used are the observations in the nadir viewing mode, from which total columns of atmospheric species can be retrieved. Regarding the limb measurements used in this study, they provide information on the vertical distributions of atmospheric trace gases and aerosols in the stratosphere. However, due to the complexity of the scattering processes associated with the detection of the solar light in the limb viewing geometry, sophisticated forward modeling and inversion approaches are required to retrieve the atmospheric composition from this kind of measurements.

Since the launch of ENVISAT in 2002, several studies have demonstrated the reliability of SCIAMACHY limb measurements of trace species involved in ozone depletion like ozone itself (e.g. von Savigny et al., 2005; Brinksma et al., 2006; Butz et al., 2006; Rozanov et al., 2007), nitrogen dioxide (e.g. Bracher et al., 2005; Rozanov et al., 2005a; Butz et al., 2006), and bromine monoxide (e.g. Rozanov et al., 2005a; Sinnhuber et al., 2005; Dorf et al., 2006; Sioris et al., 2006; Sheode et al., 2006). In case of bromine monoxide (BrO), a limited number of SCIAMACHY profiles were compared to correlative balloon measurements for verification purpose. In this paper, we present the results of the first multi-year comparison exercise of BrO vertical distributions retrieved from SCIAMACHY limb measurements (version 3.2 of the scientific product from the Institute of Environmental Physics (IUP/IFE) at the University of Bremen) and ground-based zenith-sky UV-visible observations. Based on the dependence of the mean scattering height on solar zenith angle (SZA), low vertical resolution stratospheric BrO profiles can be retrieved from ground-based UV-visible observations at twilight (e.g. Schofield et al., 2004; Hendrick et al., 2007, 2008). Given the fact that ground-based UV-visible spectrometers can be operated year-round at different sites, a great number of large data sets of BrO profiles could be potentially made available for intercomparison purpose. In the present study, we have used ground-based UV-visible measurements at three stations belonging to the Network for the Detection of Atmospheric Composition Change (NDACC; http://www.ndacc.org): Observatoire de Haute-Provence in Southern France (OHP, 44° N, 5.5° E), Harestua in Southern Nor-



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way (60° N, 11° E), and Lauder in New Zealand (45° S, 170° E). The period covered by the comparison is September 2002–October 2006 at Harestua, February 2005–November 2006 at OHP, and September 2002–October 2005 at Lauder.

The paper is divided into four parts. The SCIAMACHY limb and ground-based UV-visible BrO profile retrievals are described in the first and second parts, respectively. The third part is dedicated to the characterization of the information content in both SCIAMACHY limb and ground-based UV-visible retrievals. Finally, the comparison results are presented in the fourth part, first for both mid-latitude stations (OHP and Lauder) and secondly for the high-latitude Harestua site.

## 2 SCIAMACHY limb BrO retrieval

The vertical distribution of BrO on a global scale is retrieved at the Institute of Environmental Physics (IUP) of the University of Bremen from the measurements of the scattered solar radiation performed by the SCIAMACHY instrument in the limb viewing geometry. In the present study, the SCIAMACHY Level 1 data of version 6.03 from the European Space Agency (ESA) have been provided as input to the retrieval algorithm. A wavelength calibration has been applied and corrections for memory effect, leakage current, pixel-to-pixel gain, etalon, and internal stray light have been accounted for. The polarization correction as well as the absolute radiometric calibration have been skipped.

The profile retrieval is done using the differential two-step inversion approach implemented in the SCIATRAN software package (Rozanov at al., 2005b; Rozanov, 2008). A short description of the retrieval method is given below, whereas a more detailed description can be found in previous publications (Rozanov et al., 2005a, 2007; von Savigny et al., 2005). In this study, the version 3.2 of the retrieval algorithm has been used. This latest retrieval version uses the same inversion algorithm as earlier versions (1.x), described in the above cited papers, differing, however, quite strongly in the retrieval parameter settings. For example, a slightly different spectral range and a



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higher reference tangent height were used, Levenberg-Marquardt iterative scheme was replaced by more common Newton-type iterations, and the regularization parameters were optimized. Furthermore, additional information on pressure and temperature provided by the European Centre for Medium-Range Weather Forecasts (ECMWF) was used. A detailed list of the retrieval parameter settings for the current and previous versions of the retrieval software can be found at the data archive web page of the IUP Bremen (http://www.iup.physik.uni-bremen.de/scia-arc).

The retrieval is performed in the 338.0–356.2 nm spectral range using the normalized limb spectra, i.e. each limb spectrum measured in the selected range of tangent heights (~9–31 km) is ratioed by the limb spectrum at a higher (reference) tangent height (about 35 km in this study). Using this approach, the solar Fraunhofer structure is easily accounted for and the impact of imperfect instrument calibration is strongly reduced. To account for broadband spectral features due to unknown atmospheric parameters (e.g. albedo and aerosols), polynomials are subtracted from the normalized limb spectra at all tangent heights of interest. This procedure is similar to that of the standard DOAS (Differential Optical Absorption Spectroscopy) approach (Platt, 1994). At the first retrieval step, also referenced as the preprocessing step, a spectral fit is performed for each limb spectrum independently to find the scaling factors for the spectral corrections (in this study: tilt, ring, $I_0$, eta (polarization response); see e.g. Sioris et al. (2006) for details) as well as to account for a possible wavelength misalignment. Thereafter, all fitted corrections are applied and the main retrieval step is initiated employing the global fit method. The measurement vector comprises all spectral points in the selected spectral range obtained at all tangent heights of interest and the Optimal Estimation Method (Rodgers, 2000) is applied to obtain the vertical profiles of BrO. However, an additional smoothing constraint was introduced whereas the statistical constraint is relaxed by setting the a priori standard deviations to 25 pptv. If the corresponding value in concentration is larger than $4\times10^7$ molec/cm$^3$, the standard deviation is set to $4\times10^7$ molec/cm$^3$. The noise covariance is determined by the fit residuals at the preprocessing step. The non-linearity of the problem is accounted



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for using the Newton-type iterative approach. The simulated spectra and appropriate weighting functions are calculated using the SCIATRAN radiative transfer model which includes a fully spherical treatment of the singly scattered radiation and an approximation for the multiple scattering. The weighting functions are calculated in the single scattering approximation.

In the fit procedure, the spectral signatures of BrO, $O_3$, $NO_2$, and $O_4$ have been taken into account. The forward model was initialized using the global pressure and temperature information provided by the ECMWF and a climatological database containing monthly averaged vertical distributions of ozone and $NO_2$ (C. A. McLinden, personal communication) for 10 degree latitude bands as well as of BrO (based on MIPAS measurements; B.-M. Sinnhuber, personal communication) for 5 degree latitude bands. However, it is worth noting that the dependence on the a priori information in the sensitivity region (see Sect. 4) is insignificant (Rozanov et al., 2005a). The vertical distribution of $O_4$ was calculated using the corresponding vertical profile of the air density. Furthermore, the temperature dependent absorption cross sections of BrO obtained by the time-windowing Fourier transform spectroscopy (TW-FTS) technique (Fleischmann et al., 2004), of $O_3$ and $NO_2$ measured by the SCIAMACHY PFM Satellite Spectrometer (Bogumil et al., 2003), as well as the $O_4$ cross sections from Greenblatt et al. (1990) have been used. A background aerosol loading according to the LOWTRAN parameterization (Kneizys et al., 1986) and a constant surface albedo of 0.3 have been assumed. Clouds were completely neglected (a cloud free atmosphere is assumed for all retrievals, independently of the reality).

## 3 Ground-based UV-visible BrO retrieval

Ground-based zenith-sky UV-visible observations of BrO have been continuously performed at Harestua, OHP, and Lauder since 1998, 2005, and 1995, respectively. A description of the instrumental set-up can be found in Hendrick et al. (2007) and Theys et al. (2007) for Harestua and OHP and in Schofield et al. (2004) for Lauder. Mea-




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sured zenith radiance spectra are analysed using the DOAS technique (Platt and Stutz, 2008). Similar DOAS settings have been applied to the three data sets. In brief, the spectral signatures of $NO_2$, $O_3$, $O_4$, OClO (OHP and Lauder do not fit OClO because there is no OClO at mid-latitude), and the Ring effect have been taken into account. The retrieval of BrO at the three stations relies on the same BrO cross sections (Wilmouth et al., 1999). The fitting windows are 345–359 nm for Harestua and OHP and 342–357 nm for Lauder. More details on the DOAS settings can be found in Theys et al. (2007) and Schofield et al. (2004).

Stratospheric BrO profiles have been retrieved by applying a profiling technique to the BrO differential slant column densities (DSCDs), which are the direct product of the DOAS analysis. The profiling algorithm is based on the Optimal Estimation Method (Rodgers, 2000) and is described in Hendrick et al. (2007). It is important to note that the forward model includes a stacked box photochemical model in order to reproduce the rapid variation of BrO at twilight (see e.g. Fish et al., 1995, for a typical example of the stratospheric BrO diurnal variation at mid-latitude). Therefore, the retrieved profiles can be easily photochemically corrected to correspond to the SZA of the SCIAMACHY observations (SZA at tangent point). One should note that, because the stratospheric BrO concentration is essentially controlled by $NO_2$ through the termolecular reaction $BrO+NO_2+M \rightarrow BrONO_2$, the photochemical simulations have been constrained by the $NO_2$ profiles retrieved from simultaneous zenith-sky observations in the visible region (Hendrick et al., 2004). BrO DSCDs are evaluated using daily reference spectra, the effective residual amount of BrO in the reference spectra being directly fitted by the profiling algorithm. The term "effective" is used because the fitted quantity also includes the tropospheric contribution to the total BrO column. This makes the retrieval only sensitive to the stratosphere (Hendrick et al., 2004, 2007, 2008). At Harestua, retrievals are not performed between end of October and mid-February. During this period, the quality of the retrieval is lower, mainly because the SZA range corresponding to the BrO DSCDs is smaller (SZA at local noon can reach 84° at 60° N) and therefore the information content is somewhat lower than it is for the rest of the year (Hendrick et al.,



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2007).

## 4 Information content from SCIAMACHY limb and ground-based UV-visible retrievals

The averaging kernels matrix **A** is a key parameter in the characterization of the information content of a retrieval. The averaging kernels express the sensitivity of the retrieved profile to the true atmospheric profile (Rodgers, 2000). The FWHM (full width at half maximum) of an averaging kernel at a given altitude provides a rough estimate of the vertical resolution at this altitude and the trace of **A**, which is the number of degrees of freedom for signal, gives an estimate of the number of independent pieces of information contained in the measurements. The measurement response function can also be used to characterize a retrieval. This function is given by the area of the averaging kernels and describes how much information comes from the measurements. Values close to one indicate that most of the information comes from the measurements whereas values below 0.5 indicate a significant influence of the a priori information on the retrieved profile. Typical examples of SCIAMACHY limb and ground-based UV-visible BrO averaging kernels and measurement response functions for morning and evening retrievals are shown in Figs. 1 and 2, respectively. They correspond to the Harestua 16 April 2003 morning and 26 June 2005 evening retrievals. The evening SCIAMACHY retrievals originate from the back side of the ENVISAT orbits in late spring/summer at high latitudes and therefore are only available at Harestua. From the examination of the averaging kernels and measurement response functions, it is found that in case of SCIAMACHY limb retrievals, the altitude region with high sensitivity to the BrO vertical distribution is 15–33 km and 18–33 km for morning and evening conditions, respectively. In both cases, the vertical resolution is between 3 and 5 km. The smaller sensitivity to BrO obtained in the lower altitude levels (15–18 km) for evening retrievals is due to the fact that at large SZA, less light penetrates to the lower layers of the atmosphere leading to a worse signal to noise ratio in the limb spectra




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measured at lower tangent heights. In case of ground-based UV-visible retrievals, averaging kernels and measurement response functions are similar for both morning and evening conditions. Based on these parameters, the altitude region with high sensitivity to BrO is found to be 13–27 km. Therefore, 15–27 km and 18–27 km are the common altitude ranges chosen for morning and evening comparisons, respectively. Figure 1 also shows that the vertical resolution is 10–12 km at best for ground-based UV-visible retrievals. Averaging kernels similar to those corresponding to the Harestua 16 April 2003 morning retrieval are obtained at OHP and Lauder.

Due to the difference in vertical resolution, the SCIAMACHY profiles should be degraded to the resolution of the ground-based profiles in order to allow direct comparison (Hendrick et al., 2004, 2007). This is done by convolving the SCIAMACHY profiles with the coincident ground-based UV-visible averaging kernels using the following expression (Connor et al., 1994):

$$\mathbf{x}_{\text{sscia}} = \mathbf{x}_a + \mathbf{A}(\mathbf{x}_{\text{scia}} - \mathbf{x}_a) \quad (1)$$

where $\mathbf{A}$ is the ground-based averaging kernels matrix, $\mathbf{x}_a$ is the a priori profile used in the ground-based retrieval, $\mathbf{x}_{\text{scia}}$ is the SCIAMACHY profile, and $\mathbf{x}_{\text{sscia}}$ is the smoothed or convolved SCIAMACHY profile which represents what the retrieval should produce assuming that $\mathbf{x}_{\text{scia}}$ is the true profile and that the only source of error is the smoothing error.

According to the smoothing method used (see Eq. 1), SCIAMACHY profiles have to be extended to the same altitude grid as the ground-based UV-visible averaging kernels. In the present study, the SCIAMACHY profiles have been completed below and above the covered altitude range by the ground-based a priori profiles scaled by the ratios between the retrieved SCIAMACHY and ground-based a priori profiles at the lower and upper altitude limits of the SCIAMACHY profiles, respectively. This scaling prevents from the occurence of discontinuities at the lower and upper altitude limits of the SCIAMACHY profiles (Hendrick et al., 2004). However, it should be noted that this smoothing method introduces an additional uncertainty above ~25 km and especially below ~18 km which is related to the SCIAMACHY profiles extrapolation procedure.



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The number of independent pieces of information in both SCIAMACHY and ground-based UV-visible measurements has been estimated. The values of the trace of **A** are about 4.5 and 3.5 for SCIAMACHY morning and evening retrievals, respectively, while it reaches 2.5 for ground-based UV-visible retrievals (these values are given for the whole stratosphere).

## 5 Comparison results

In this section, stratospheric BrO profiles and corresponding partial columns retrieved from ground-based UV-visible measurements at Harestua, OHP, and Lauder are compared to coincident SCIAMACHY limb data. One should note that in all comparison plots, ground-based data are arbitrarily taken as reference for the calculation of relative differences. As discussed in Sect. 4, comparison results are shown for the 15–27 km altitude range, except for Harestua evening coincidences where the 18–27 km altitude range is used. BrO partial columns are calculated by integrating the vertical profiles in these altitude ranges. For the selection of the SCIAMACHY profiles, the following spatial coincidence criterion is chosen: the average latitude and longitude at tangent point should fall within latitude of the stations ±5° and longitude of the stations ±10°. Concerning the temporal criterion, the photochemical model PSCBOX included in the profiling algorithm (see Sect. 3) is used to convert the ground-based profiles to values appropriate to the SZA at the tangent point area of the coincident SCIAMACHY limb observations. This ensures photochemical matching, within the accuracy of the photochemical model, for both SCIAMACHY and ground-based profiles. This is an important criterion when comparing measurements of species having a strong diurnal variation such as BrO. However, because of differences in the local time of the observations (typically 3 h in winter and up to 6 (OHP and Lauder) and 8 h (Harestua) around the summer solstice), an uncertainty due to possible dynamical fluctuations still remains. When applying these criteria, we found 265 morning coincidences events at OHP for the February 2005–November 2006 period. At Harestua, 561 coincidences have been selected



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for September 2002–October 2006 period, including 512 morning coincidences and 49 evening coincidences. It should be noted that in case of evening coincidences, SCIAMACHY and ground-based measurements occur at almost the same local time, i.e. around 85° SZA. At Lauder, we found 517 morning coincidences for the September 2002–October 2005 period.

## 6 OHP and Lauder

Figures 3 and 4 show the comparison between mean SCIAMACHY and ground-based UV-visible BrO profiles at OHP and Lauder, respectively. A reasonably good agreement is found in the whole 15–27 km altitude range with relative difference smaller than 21%. At OHP, the ground-based profile is lower than SCIAMACHY between 15 and 20 km while the opposite is found above 20 km. At Lauder, the ground-based profile is systematically lower than SCIAMACHY in the 15.5–26.5 km altitude range with a maximum relative difference of +19% around 21 km. In the 18–27 km altitude range, the ground-based UV-visible retrieval gives significantly lower BrO concentration values at Lauder than at OHP, while the corresponding SCIAMACHY profiles are very close. This could be related to the use of not strictly identical DOAS settings for both stations, which can lead to differences in the DSCDs and their corresponding errors. Below 18 km, we see from Figs. 3 and 4 that the unsmoothed SCIAMACHY profile shows significantly lower BrO concentration values at Lauder than at OHP. Because of the 8–10 km vertical resolution of the ground-based profiles, the agreement with the smoothed SCIAMACHY profiles in the lower layers (15–20 km) could be influenced by the smoothing method used, in particular by the way the SCIAMACHY profiles are extended to the ground (see Sect. 4).

Comparison results for the 15–27 km BrO partial columns at OHP and Lauder are depicted in Figs. 5 and 6, respectively. At OHP, the agreement between SCIAMACHY and ground-based columns is very good with SCIAMACHY being higher than the ground-based observations by 1±18% on average and SCIAMACHY data are most of the




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time within the error bars associated to the ground-based columns (corresponding to the total error (systematic + random errors) calculated as in Hendrick et al., 2007). At Lauder, a larger discrepancy is obtained, with SCIAMACHY being higher than the ground-based observations by 11±16% on average. One should note that an additional bias of up to 10% is expected in the comparison results if the same BrO cross-sections would have been used in both SCIAMACHY and ground-based UV-visible retrievals (this remark is also valid for profile and column comparisons for the Harestua station). The seasonality of BrO, directly related to the $NO_2$ seasonal cycle, is also consistently captured at both stations by both SCIAMACHY and ground-based UV-visible retrievals. In both SCIAMACHY and ground-based UV-visible data sets, the BrO seasonality is less marked at Lauder than at OHP, with larger BrO column values in winter at OHP than at Lauder. Since the main driver for the BrO seasonality is the $NO_2$ seasonal cycle, we have examined the $NO_2$ 15–27 km partial columns seasonal cycle at both stations derived from SCIAMACHY limb profiles (version 3.1 of the IUP Bremen scientific product; see e.g. Bracher et al., 2005, and Rozanov et al., 2005a). Figure 7 shows that in winter, $NO_2$ partial columns are significantly lower at OHP than at Lauder (by about 30% in average). Less $NO_2$ at OHP means less $BrONO_2$ and therefore more HOBr as bromine reservoir. Since HOBr is photolyzed more rapidly than $BrONO_2$, this can at least partly explain the larger BrO column values in winter at OHP and therefore the more marked stratospheric BrO seasonality at this station. Figures 5 and 6 also show that the relative difference between SCIAMACHY and ground-based UV-visible BrO partial columns has a marked seasonal dependence, with a tendency to have smaller or negative relative difference values in summer than during the rest of the year. This seasonality is most probably related to the difference in the local time of both SCIAMACHY and ground-based observations (performed around 10:00 h local time and at twilight (80–93°SZA), respectively). At OHP and Lauder, this difference is of about 3 h in winter and can reach up to 6 h at the summer solstice. Therefore, a larger impact of the photochemical correction applied to the ground-based profiles is expected in summer. This photochemical correction depends mainly on the accuracy of the $NO_2$



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profiles used to initialize the stacked box photochemical model and on the uncertainties of the reaction rates. As mentioned in Sect. 3, stratospheric $NO_2$ profiles retrieved from simultaneous zenith-sky observations in the visible region have been used. The accuracy of the columns corresponding to these profiles is about 10% (Hendrick et al., 2004). Since $NO_2$ columns display a strong seasonality with a maximum in summer and a minimum in winter, one can expect in late spring/summer a larger impact of this parameter on the photochemically corrected BrO profiles and corresponding columns. This is confirmed by sensitivity tests performed for the three stations using the stacked box photochemical model PSCBOX. We found that an uncertainty of 10% in the stratospheric $NO_2$ columns has an impact of 2% on the 15–27 km BrO partial column in winter, while this impact reaches 5% of the BrO partial column values in summer. Model calculations have also shown that the impact of the rate uncertainty of the termolecular reaction $BrO+NO_2+M$ displays a seasonality: an impact of 4% or less on the retrieved BrO partial columns is found in winter at both stations, while this impact is around 10% in summer. The seasonality in the agreement between SCIAMACHY and ground-based UV-visible BrO partial columns could also be partly related to the SCIAMACHY observation geometry, namely, due to the variation of the SZA at tangent point throughout the year (significantly smaller SZA values in summer than in winter/early spring). Smaller SZA values in summer mean indeed more light due to shorter light paths from the Sun to the scattering point. Therefore, for SCIAMACHY measurements in summer, a better signal to noise ratio is measured and, thus, a better sensitivity to the lower layers as compared to the winter measurements performed at higher SZA.

## 7 Harestua

Morning BrO profiles have been averaged separately for late winter/early spring and late spring/summer/early fall periods because in late winter/early spring, large stratospheric BrO enhancement events associated to chlorine activation regularly occur over




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Harestua when the polar vortex is present. The number of coincidences for both periods is 154 and 358, respectively. Figure 8 shows the comparison results of mean ground-based and SCIAMACHY morning profiles. For both periods the agreement is very good between 15 and 22 km with relative differences having a slight positive bias and maximum value of +6% in late winter/early spring and a slight negative bias and maximum value of −8% in late spring/summer/early fall. Above 21–22 km, the ground-based retrieval gives larger BrO concentration values than SCIAMACHY with a maximum difference of about −20% at 27 km for both late winter/early spring and late spring/summer/early fall periods. Comparison results for evening coincidences are depicted in Fig. 9. SCIAMACHY and ground-based profiles agree well, with SCIAMACHY smaller than ground-based by less than 6% between 18 and 27 km of altitude. The better agreement found for evening coincidences is most probably due to the fact that both SCIAMACHY and ground-based measurements are performed at almost the same local time. This minimizes the effect of possible dynamical fluctuations between both measurements and the impact on the agreement of the uncertainty in the photochemical correction applied to ground-based profiles is also expected to be smaller.

The BrO partial columns corresponding to morning and evening coincidences are presented in Figs. 10 and 11, respectively. Both morning and evening comparisons show that the SCIAMACHY and ground-based BrO columns are in good agreement, with, in average, SCIAMACHY lower than ground-based by −2±19% and higher by +4±13%, respectively. The SCIAMACHY data are also generally within the error bars associated to the ground-based columns (corresponding to the total error), especially for evening conditions. The morning comparison displays similar features as at OHP and Lauder: (1) A seasonality in the relative difference, with a tendency to have smaller or negative relative difference values in summer than during the rest of the year. As discussed in Sect. 5.1, this is most probably related to the uncertainty in the photochemical correction applied to ground-based profiles. Performing the same sensitivity tests as for OHP and Lauder, it is found that this uncertainty is larger at Harestua because of the presence of larger amount of $NO_2$ in the stratosphere at 60° N than at



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mid-latitude. (2) The very good consistency in both data sets regarding the capture of the seasonality in the BrO column. Comparison results in late winter/early spring 2005 and 2006 also show that large BrO column values associated with chlorine activation events are consistently detected by both instruments.

## 8 Conclusions

We have presented the results of the first multi-year (2002–2006) comparison of stratospheric BrO profiles retrieved from SCIAMACHY limb (version 3.2 of the IUP Bremen scientific product) and ground-based UV-visible measurements performed over Harestua (60° N), OHP (44° N), and Lauder (45° S). A comparison of the SCIAMACHY limb and ground-based UV-visible averaging kernels has shown that 15–27 km (morning coincidences) and 18–27 km (evening coincidences at Harestua) are the common altitude ranges where both retrievals display significant information content on the vertical distribution of BrO. A good agreement is found between SCIAMACHY limb and ground-based UV-visible partial columns calculated by integrating the retrieved profiles in the appropriate altitude range: at Harestua, SCIAMACHY is lower than the ground-based observations by 2±19% and higher by 4±13% on average for morning and evening coincidences, respectively. At OHP and Lauder (morning coincidences), SCIAMACHY is larger than the ground-based observations by 1±18% and 11±16%, respectively. At the three stations, the relative difference between both data sets show a marked seasonal dependence, with a tendency to have SCIAMACHY generally larger than the ground-based observations in fall/winter/early spring and lower in late spring/summer. This seasonal dependence in the agreement is most probably caused by the stronger influence in summer of the photochemical correction applied to the ground-based profiles. Nevertheless, the seasonality on the BrO column is still consistently captured in both SCIAMACHY and ground-based UV-visible observations. Furthermore, large BrO columns associated with chlorine activation events are simultaneously detected by both instruments in winter/early spring at Harestua. When



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comparing the mean vertical profiles, we have found a maximum difference of 23% between SCIAMACHY and ground-based UV-visible profiles. At OHP and Harestua, ground-based UV-visible retrievals give larger BrO concentration values than SCIAMACHY above 20–22 km while the opposite behaviour is found below 20 km, except for Harestua in late spring/summer/early fall where ground-based UV-visible is larger than SCIAMACHY also in the 15–20 km altitude range. At Lauder, SCIAMACHY tends to be systematically larger than the ground-based observations between 15 and 27 km.

In summary, this comparison study highlights the consistency and stability of the SCIAMACHY limb and ground-based UV-visible BrO profile retrievals and the capability to use these data sets for geophysical studies, i.e. for analyzing spatial and temporal variations of stratospheric BrO.

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## References

Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O. C., Vogel, A., Hartmann, M., Bovensmann, H., Frerik, J., and Burrows, J. P.: Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and

reference data for atmospheric remote sensing in the 230–2380 nm region, J. Photochem. Photobiol. A., 157, 167–184, doi:10.1016/S1010-6030(03)00062-5, 2003.
Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goede, A. H. P.: SCIAMACHY – Mission Objectives and Measurement Modes, J. Atmos. Sci., 56, 127–150, 1999.
Bracher, A., Sinnhuber, M., Rozanov, A., and Burrows, J. P.: Using a photochemical model for the validation of $NO_2$ satellite measurements at different solar zenith angles, Atmos. Chem. Phys., 5, 393–408, 2005, http://www.atmos-chem-phys.net/5/393/2005/.
Brinksma, E. J., Bracher, A., Lolkema, D. E., Segers, A. J., Boyd, I. S., Bramstedt, K., Claude, H., Godin-Beekmann, S., Hansen, G., Kopp, G., Leblanc, T., McDermid, I. S., Meijer, Y. J., Nakane, H., Parrish, A., von Savigny, C., Stebel, K., Swart, D. P. J., Taha, G., and Piters, A. J. M.: Geophysical validation of SCIAMACHY Limb Ozone Profiles, Atmos. Chem. Phys., 6, 197–209, 2006, http://www.atmos-chem-phys.net/6/197/2006/.
Butz, A., Bösch, H., Camy-Peyret, C., Chipperfield, M., Dorf, M., Dufour, G., Grunow, K., Jeseck, P., Kühl, S., Payan, S., Pepin, I., Pukite, J., Rozanov, A., von Savigny, C., Sioris, C., Wagner, T., Weidner, F., and Pfeilsticker, K.: Inter-comparison of stratospheric $O_3$ and $NO_2$ abundances retrieved from balloon borne direct sun observations and Envisat/SCIAMACHY limb measurements, Atmos. Chem. Phys., 6, 1293–1314, 2006, http://www.atmos-chem-phys.net/6/1293/2006/.
Connor, B. J., Siskind, D. E., Tsou, J. J., Parrish, A., and Remsberg, E. E.: Ground-based microwave observations of ozone in the upper stratosphere and mesosphere, J. Geophys. Res., 99(D8), 16757–16770, 1994.
Dorf, M., Bösch, H., Butz, A., Camy-Peyret, C., Chipperfield, M. P., Engel, A., Goutail, F., Grunow, K., Hendrick, F., Hrechanyy, S., Naujokat, B., Pommereau, J.-P., Van Roozendael, M., Sioris, C., Stroh, F., Weidner, F., and Pfeilsticker, K.: Balloon-borne stratospheric BrO measurements: comparison with Envisat/SCIAMACHY BrO limb profiles, Atmos. Chem. Phys., 6, 2483–2501, 2006, http://www.atmos-chem-phys.net/6/2483/2006/.
Fish, D. J., Jones, R. L., and Strong, E. K.: Midlatitude observations of the diurnal variation of stratospheric BrO, J. Geophys. Res., 100(D9), 18863–18871, 1995.
Fleischmann, O. C., Hartmann, M., Burrows J. P., and Orphal, J.: New ultraviolet absorption cross-sections of BrO at atmospheric temperatures measured by time-windowing Fourier transform spectroscopy, J. Photochem. Photobiol. A, 168, 117–132, 2004.
Greenblatt, G. D., Orlando, J. J., Burkholder, J. B., and Ravishankara, A. R.: Absorption mea-

surements of oxygen between 330 and 1140 nm, J. Geophys. Res., 95, 18577–18582, 1990.
Hendrick, F., Barret, B., Van Roozendael, M., Boesch, H., Butz, A., De Mazière, M., Goutail, F., Hermans, C., Lambert, J.-C., Pfeilsticker, K., and Pommereau, J.-P.: Retrieval of nitrogen dioxide stratospheric profiles from ground-based zenith-sky UV-visible observations: validation of the technique through correlative comparisons, Atmos. Chem. Phys., 4, 2091–2106, 2004, http://www.atmos-chem-phys.net/4/2091/2004/.
Hendrick, F., Van Roozendael, M., Chipperfield, M. P., Dorf, M., Goutail, F., Yang, X., Fayt, C., Hermans, C., Pfeilsticker, K., Pommereau, J.-P., Pyle, J. A., Theys, N., and De Mazière, M.: Retrieval of stratospheric and tropospheric BrO profiles and columns using ground-based zenith-sky DOAS observations at Harestua, 60° N, Atmos. Chem. Phys., 7, 4869–4885, 2007, http://www.atmos-chem-phys.net/7/4869/2007/.
Hendrick, F., Johnston, P. V., De Mazière, M., Fayt, C., Hermans, C., Kreher, K., Theys, N., Thomas, A., and Van Roozendael, M.: 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, 2008.
Kneizys, F. X., Shettle, E. P., Abreu, L. W., Chetwynd, J. H., Anderson, G. P., Gallery, W. O., Selby, J. E. A., and Clough, S. A.: Users Guide to LOWTRAN 7, Technical report, Air Force Geophysics Laboratory AFGL, 1986.
Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy (DOAS), Principles and Applications, ISBN 978-3-540-21193-8, Springer, Berlin Heidelberg, 2008.
Rodgers, C. D.: Inverse Methods for Atmospheric Sounding, Theory and Practice, World Scientific Publishing, Singapore-NewJersey-London-Hong Kong, 2000.
Rozanov, A., Bovensmann, H., Bracher, A., Hrechanyy, S., Rozanov, V., Sinnhuber, M., Stroh, F., and Burrows, J.: $NO_2$ and BrO vertical profiles retrieval from SCIAMACHY limb measurements: Sensitivity studies, Adv. Space Res., 36, 846–854, doi:10.1016/j.asr.2005.03.013, 2005a.
Rozanov, A., Rozanov, V., Buchwitz, M., Kokhanovsky, A., and Burrows, J. P.: SCIATRAN 2.0 – A new radiative transfer model for geophysical applications in the 175–2400 nm spectral region, Adv. Space Res., 36, 1015–1019, doi:10.1016/j.asr.2005.03.012, 2005b.
Rozanov, A., Eichmann, K.-U., von Savigny, C., Bovensmann, H., Burrows, J. P., von Bargen, A., Doicu, A., Hilgers, S., Godin-Beekmann, S., Leblanc, T., and McDermid, I. S.: Comparison of the inversion algorithms applied to the ozone vertical profile retrieval from SCIAMACHY limb measurements, Atmos. Chem. Phys., 7, 4763–4779, 2007,

http://www.atmos-chem-phys.net/7/4763/2007/.
Rozanov, A.: SCIATRAN: Radiative transfer model and retrieval software package, http://www.iup.physik.uni-bremen.de/sciatran, 2008.
Schofield, R., Kreher, K., Connor, B. J., Johnston, P. V., Thomas, A., Shooter, D., Chipperfield, M. P., Rodgers, C. D., and Mount, G. H.: Retrieved tropospheric and stratospheric BrO columns over Lauder, New Zealand, J. Geophys. Res., 109, D14304, doi:10.1029/2003JD004463, 2004.
Sheode, N., Sinnhuber, B.-M., Rozanov, A., and Burrows, J. P.: Towards a climatology of stratospheric bromine monoxide from SCIAMACHY limb observations, Atmos. Chem. Phys. Discuss., 6, 6431–6466, 2006, http://www.atmos-chem-phys-discuss.net/6/6431/2006/.
Sinnhuber, B.-M., Rozanov, A., Sheode, N., Afe, O. T., Richter, A., Sinnhuber, M., Wittrock, F., Burrows, J. P., Stiller, G. P., von Clarmann, T., and Linden, A.: Global observations of stratospheric bromine monoxide from SCIAMACHY, Geophys. Res. Lett., 32, L20810, doi:10.129/2005GL023839, 2005.
Sioris, C. E., Kovalenko, L. J., McLinden, C. A., Salawitch, R. J., Van Roozendael, M., Goutail, F., Dorf, M., Pfeilsticker, K., Chance, K., von Savigny, C., Liu, X., Kurosu, T. P., Pommereau, J.-P., Bösch, H., and Frerick, J.: Latitudinal and vertical distribution of bromine monoxide in the lower stratosphere from Scanning Imaging Absorption Spectrometer for Atmospheric Chartography limb scattering measurements, J. Geophys. Res., 111, D14301, doi:10.1029/2005JD006479, 2006.
Theys, N., Van Roozendael, M., Hendrick, F., Fayt, C., Hermans, C., Baray, J.-L., Goutail, F., Pommereau, J.-P., and De Mazière, M.: Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21° S, 56° E), Atmos. Chem. Phys., 7, 4733–4749, 2007, http://www.atmos-chem-phys.net/7/4733/2007/.
von Savigny, C., Rozanov, A., Bovensmann, H., Eichmann, K.-U., Noel, S., Rozanov, V. V., Sinnhuber, B.-M.,Weber, M., Burrows, J. P., and Kaiser, J. W.: The ozone hole break-up in September 2002 as seen by SCIAMACHY on ENVISAT, J. Atmos. Sci., 62, 721–734, doi:10.1175/JAS-3328.1, 2005.
Wilmouth, D. M., Hanisco, T. F., Donahue, N. M., and Anderson, J. G.: 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, 1999.

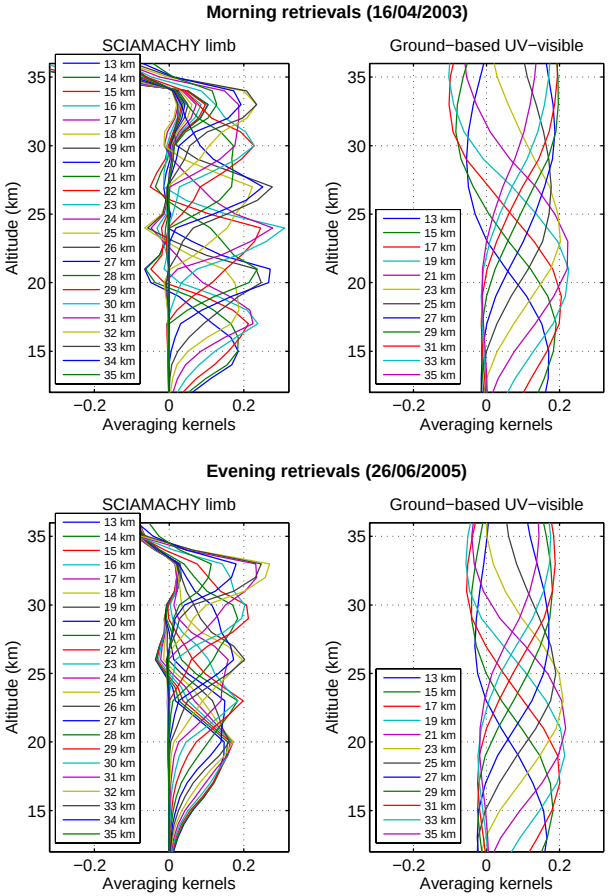


**Fig. 1.** Typical examples of averaging kernels for morning (upper plots) and evening (lower plots) SCIAMACHY limb and ground-based UV-visible BrO retrievals. They correspond to the Harestua 16 April 2003 morning and 26 June 2005 evening retrievals.



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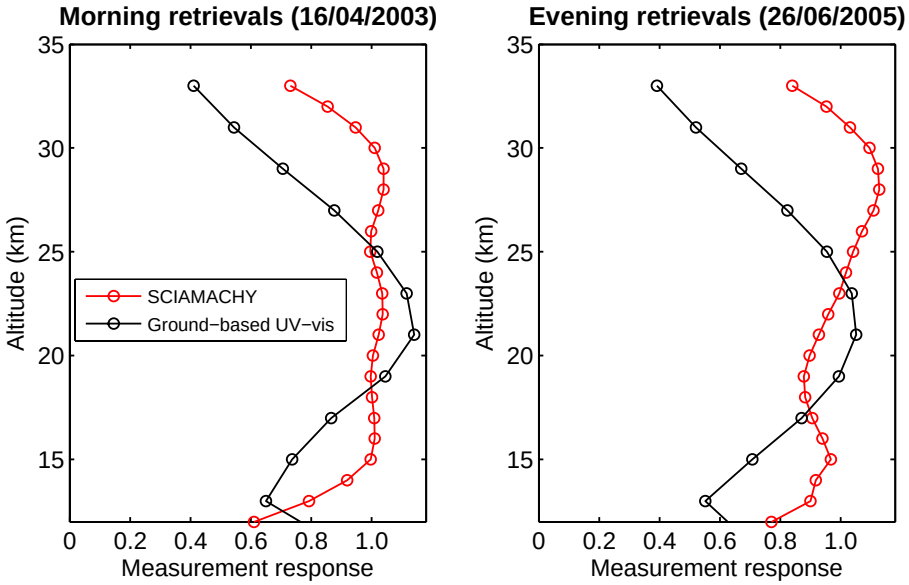


**Fig. 2.** Typical examples of measurement response functions for morning (left plot) and evening (right plot) SCIAMACHY limb and ground-based UV-visible BrO retrievals. They correspond to the Harestua 16 April 2003 morning and 26 June 2005 evening retrievals.



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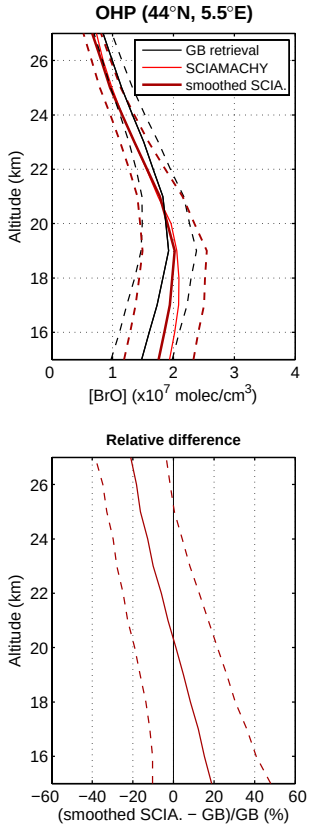


**Fig. 3.** Comparison between mean SCIAMACHY limb (thin red and thick dark red solid lines) and ground-based UV-visible BrO profiles (solid black line) at OHP (44° N, 5.5° E) for morning conditions for the 2005–2006 period (265 coincidences). The mean relative differences appear in the lower plot. They have been plotted for the smoothed SCIAMACHY profile. In both plots, the dashed lines represent the one-sigma standard deviation.



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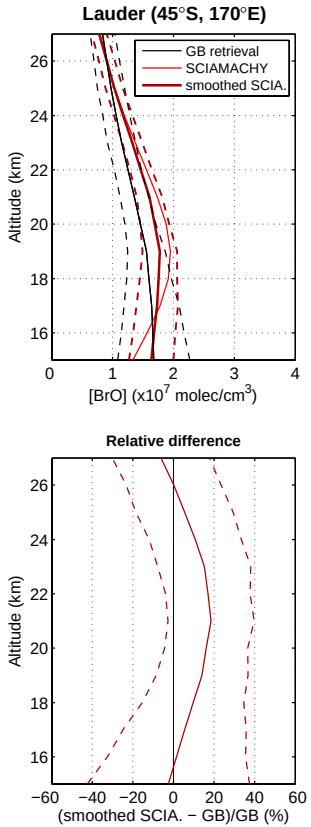


**Fig. 4.** Comparison between mean SCIAMACHY limb (thin red and thick dark red solid lines) and ground-based UV-visible BrO profiles (solid black line) at Lauder (45° S, 170° E) for morning conditions for the 2002–2005 period (517 coincidences). The mean relative differences appear in the lower plot. They have been plotted for the smoothed SCIAMACHY profile. In both plots, the dashed lines represent the one-sigma standard deviation.



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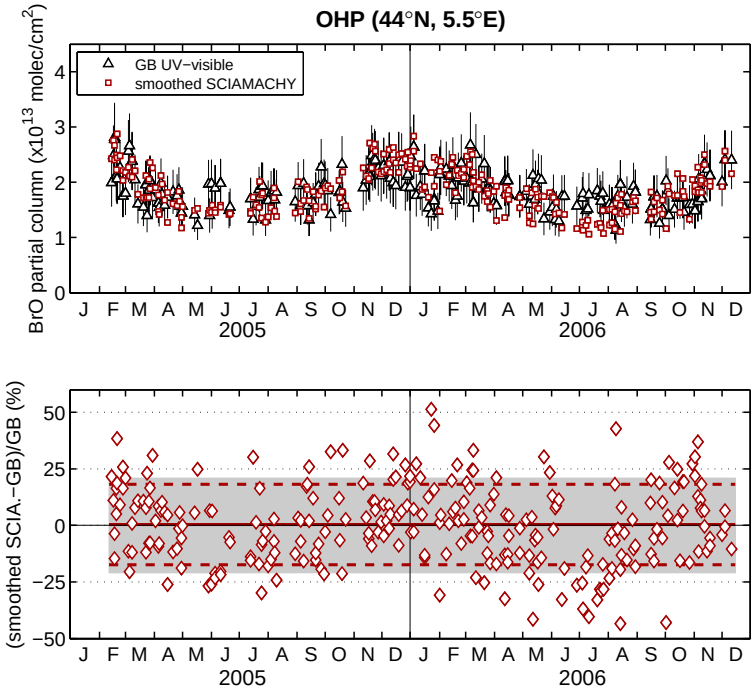


**Fig. 5.** Comparison of the 15–27 km BrO partial columns calculated from the smoothed SCIAMACHY limb and ground-based UV-visible profiles at OHP (44° N, 5.5° E) for the 2005–2006 period (morning coincidences). The relative differences appear on the lower plot. The error bars on the ground-based data correspond to the total error (systematic error + total retrieval error), estimated as in Hendrick et al. (2007). The solid and dashed red lines in the lower plot correspond to the mean relative difference and its one-sigma standard deviation, respectively. The grey-shaded area indicates the mean uncertainty region for the ground-based UV-visible partial columns.



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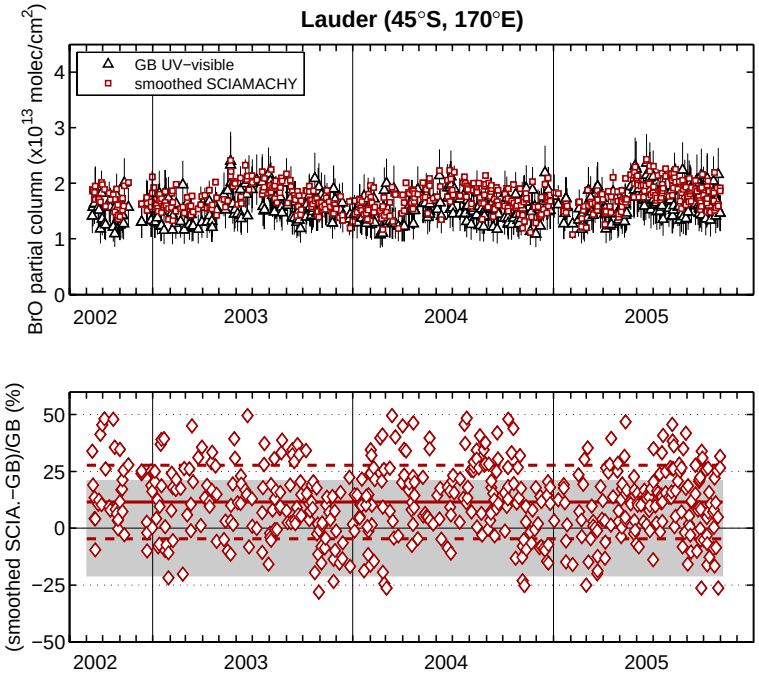


**Fig. 6.** Comparison of the 15–27 km BrO partial columns calculated from the smoothed SCIAMACHY limb and ground-based UV-visible profiles at Lauder (45° S, 170° E) for the 2002–2005 period (morning coincidences). The relative differences appear on the lower plot. The error bars on the ground-based data correspond to the total error (systematic error + total retrieval error), estimated as in Hendrick et al. (2007). The solid and dashed red lines in the lower plot correspond to the mean relative difference and its one-sigma standard deviation, respectively. The grey-shaded area indicates the mean uncertainty region for the ground-based UV-visible partial columns.



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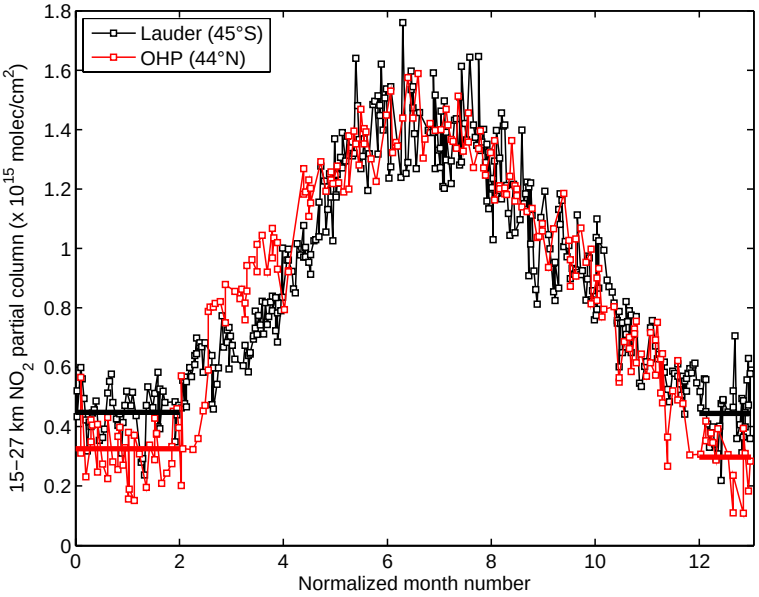


**Fig. 7.** Typical 15–27 km $NO_2$ partial column seasonal cycle at Lauder (45° S, 170° E) and OHP (44° N, 5.5° E) derived from SCIAMACHY limb profiles. At Lauder, month 0 corresponds to June 2003 and month 12 to June 2004. At OHP, month 0 corresponds to December 2005 and month 12 to December 2006. Thick solid lines correspond to mean partial columns for the months 0–2 and month 12 periods (red OHP; black: Lauder).



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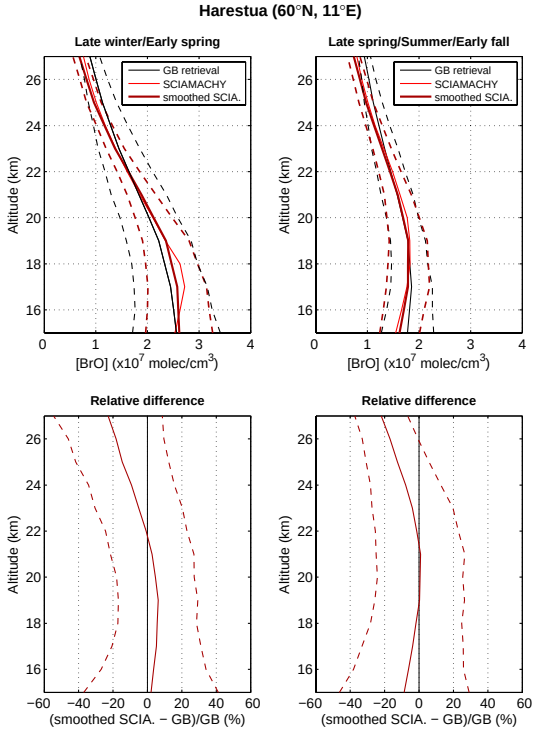


**Fig. 8.** Comparison between mean SCIAMACHY limb (thin red and thick dark red solid lines) and ground-based UV-visible BrO profiles (solid black line) at Harestua (60° N, 11° E) for the 2002–2006 period (morning coincidences). Profiles have been plotted separately for late winter/early spring (left plot) and late spring/summer/early fall (right plot) conditions. The number of coincident events is 154 and 358, respectively. The mean relative differences appear in the lower plots. They have been plotted for the smoothed SCIAMACHY profiles. In the four plots, the dashed lines represent the one-sigma standard deviation.



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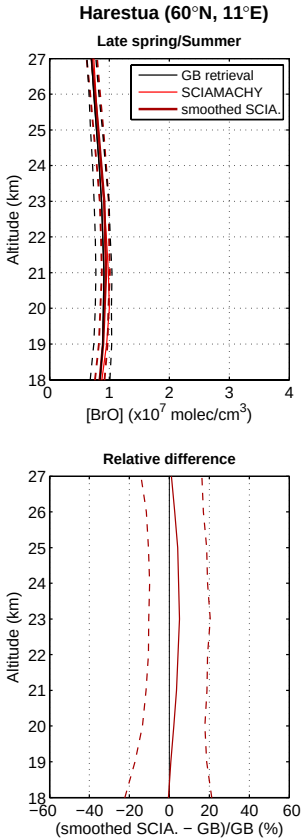


**Fig. 9.** Comparison between mean SCIAMACHY limb (thin red and thick dark red solid lines) and ground-based UV-visible BrO profiles (solid black line) at Harestua (60° N, 11° E) for evening conditions for the 2002–2006 period (49 coincidences). The mean relative differences appear in the lower plot. They have been plotted for the smoothed SCIAMACHY profile. In both plots, the dashed lines represent the one-sigma standard deviation.



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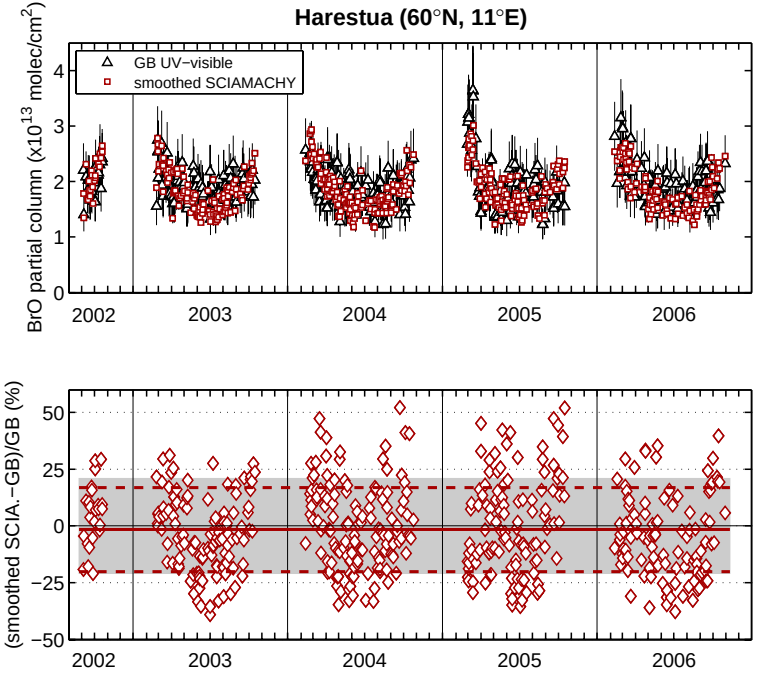


**Fig. 10.** Comparison of the 15–27 km BrO partial columns calculated from the smoothed SCIAMACHY limb and ground-based UV-visible profiles at Harestua (60° N, 11° E) for the 2002–2006 period (morning coincidences). The relative differences appear on the lower plot. The error bars on the ground-based data correspond to the total error (systematic error + total retrieval error), estimated as in Hendrick et al. (2007). The solid and dashed red lines in the lower plot correspond to the mean relative difference and its one-sigma standard deviation, respectively. The grey-shaded area indicates the mean uncertainty region for the ground-based UV-visible partial columns.



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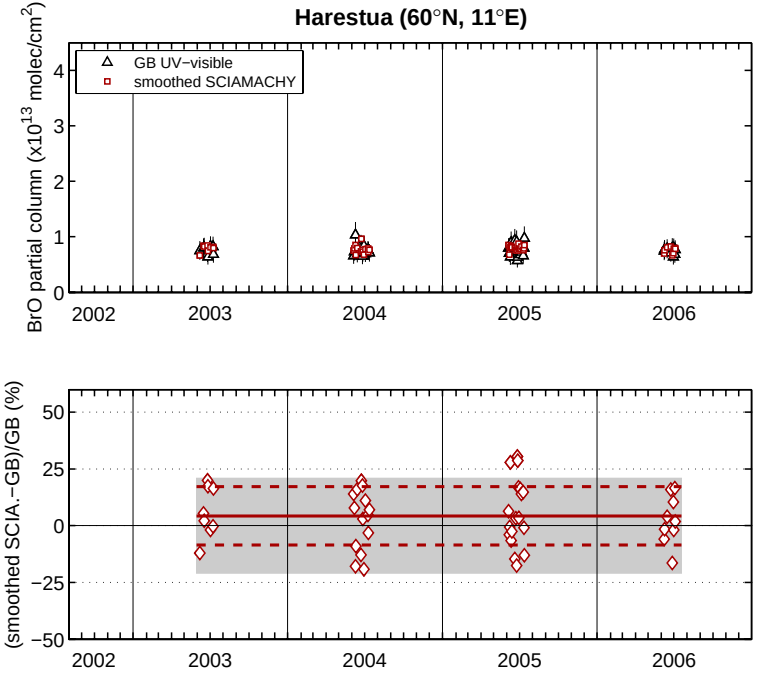


**Fig. 11.** Comparison of the 18–27 km BrO partial columns calculated from the smoothed SCIAMACHY limb and ground-based UV-visible profiles at Harestua (60° N, 11° E) for the 2002–2006 period (evening coincidences). The relative differences appear on the lower plot. The error bars on the ground-based data correspond to the total error (systematic error + total retrieval error), estimated as in Hendrick et al. (2007). The solid and dashed red lines in the lower plot correspond to the mean relative difference and its one-sigma standard deviation, respectively. The grey-shaded area indicates the mean uncertainty region for the ground-based UV-visible partial columns.



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