

# CURRENT RETRIEVAL AND INTER-COMPARISONS RESULTS OF SCIAMACHY NIGHTTIME NO<sub>x</sub>

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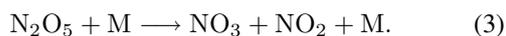
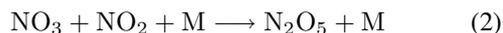
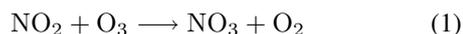
## ABSTRACT

Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) performs lunar occultation measurements over the high southern latitude (50° S–90° S). Using the global spectra fitting method by the differential optical depth approach and the optimal estimation method, vertical profiles of nighttime NO<sub>x</sub> (NO<sub>2</sub> and NO<sub>3</sub>) are retrieved. The quality of the retrieved NO<sub>x</sub> products are verified by comparing SCIAMACHY nighttime NO<sub>2</sub> result with other satellite instruments (HALOE and SAGE II) and NO<sub>3</sub> results with a simple chemical model outputs. Very promising results are obtained. The relative mean differences (rmd) of SCIAMACHY-HALOE comparisons are within -16 % to +3 % and the standard deviations (rms) within 4–16 % between 25–38 km. The rmd and rms for SCIAMACHY-SAGE II comparisons are within -9 % to +7 % and 10–17 % between 22–39 km. The retrieved NO<sub>3</sub> are in very good agreement with the model calculations between 16 to 38 km within accuracy of 25 %.

Key words: stratospheric NO<sub>x</sub>; NO<sub>2</sub>; NO<sub>3</sub>; validation; SCIAMACHY; lunar occultation.

## 1. INTRODUCTION

O<sub>3</sub>, NO<sub>2</sub>, and NO<sub>3</sub> are key molecules involve in nighttime stratospheric chemistry. The major nighttime reactions involving these molecules are:



Observations of stratospheric nighttime NO<sub>x</sub> (NO<sub>2</sub> and NO<sub>3</sub>) employing lunar occultation method began in the late 1970s with ground based instruments (Noxon et al., 1978). Similar measurements were performed in the 1980 and 1990s (Platt et al., 1980; Sander et al., 1987;

Solomon et al., 1993). The lunar occultation measurement technique is used for the first time to measure trace gases abundance by satellite instruments; the Scanning Imaging Absorption SCIAMACHY on ENVISAT (launched in March 2002) (Bovensmann et al., 1999) and the Stratospheric Aerosol and Gas Experiment III (SAGE III) on Meteor-3M (lunched in December 2001) (McCormick et al., 2002).

SCIAMACHY instrument performs lunar occultation measurements in the southern hemisphere between 30°–90° during local nighttime in moon pointing mode, when the phase of the moon is about 0.6 and end shortly after full moon. The measurements duration is about 6–8 days per month and 4–8 months in the year, yielding at least 300 vertical profiles per year of nighttime stratospheric trace gases (O<sub>3</sub>, NO<sub>2</sub> and NO<sub>3</sub>). The integration time for the lunar occultation measurements is 1.0 s and the vertical resolution is approximately 2.5 km. The horizontal resolution is 30 km across track and extending approximately 400 km along track. Detailed information on SCIAMACHY lunar occultation measurements is provided in Amekudzi (2005); Amekudzi et al. (2005b).

The aim of this paper is to present the recent retrieval results of SCIAMACHY lunar occultation NO<sub>2</sub> and NO<sub>3</sub> vertical profiles. We provide information on the improved SCIAMACHY lunar occultation NO<sub>2</sub> and NO<sub>3</sub> data analysis scheme in Section 2. The NO<sub>2</sub> retrieval and comparisons with HALOE and SAGE II results are presented in Section 3. The retrieval and comparisons with model results of NO<sub>3</sub> are presented in Section 4 and important findings are summarized in Section 5.

## 2. DATA ANALYSIS PROCEDURE

The SCIAMACHY lunar occultation version 2.1 NO<sub>x</sub> products reported in Amekudzi et al. (2005a,b) and Amekudzi (2005) were retrieved from the level-0 (uncalibrated) data using GOMETRAN occultation retrieval code. The current NO<sub>x</sub> (i.e. version 2.2) products are retrieved from level-1b version 5.04 using the SCIATRAN version 2.1 code (Rozanov et al., 2005). The major differences between the two codes are described in Amekudzi et al. (2007).

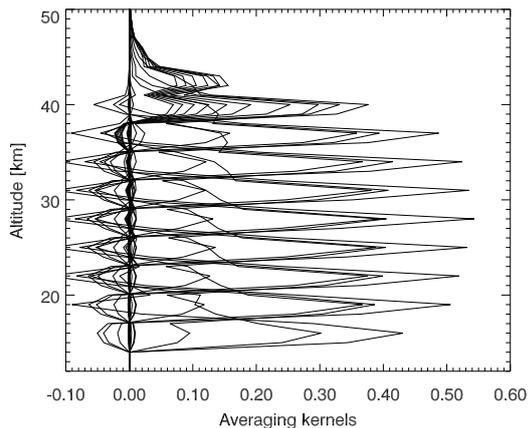


Figure 1.  $\text{NO}_2$  averaging kernels for the retrieval altitude 18–48 km for orbit 05402, measurement day 13/03/2003, UTC time 12:17:55.

$\text{NO}_2$  is retrieved mainly from 430–460 nm by simultaneously fitting of  $\text{NO}_2$  and  $\text{O}_3$  using the global fitting and the differential optical depth method. Similar method is used to retrieve  $\text{NO}_3$  by utilizing the most prominent  $\text{NO}_3$  absorption band at 623 nm  $\nu_1(1,0)$  and 662 nm  $\nu_1(0,0)$ . These absorption bands, however have significant contributions from other absorbers such as  $\text{O}_3$ ,  $\text{O}_2$ ,  $\text{O}_4$ , and  $\text{H}_2\text{O}$ . To accurately fit and retrieve  $\text{NO}_3$  profiles, these interfering gases were fitted in addition to  $\text{NO}_3$ .  $\text{O}_2$  and  $\text{H}_2\text{O}$  are line absorber, their absolute cross sections are calculated by using the exponential sum fitting of transmittances (ESFT) method (Buchwitz et al., 2000). we find the ESFT as a better alternative to the line-by-line method used in version 2.1 retrieval code (Amekudzi, 2005; Amekudzi et al., 2005b), as it requires less computing time and provides a more accurate spectral fit at the lower tangent heights (below 22 km).

In both  $\text{NO}_2$  and  $\text{NO}_3$  retrieval scheme, broadband absorption features of the atmosphere and instrument are removed from the measured spectra by subtracting a third order polynomial. A signal to-noise-ratio of 1500 were used in both scheme. Twomey-Tikhonov regularization procedure is applied to smooth the retrieved profiles. The tangent height information derived from the improved misalignment angles for the SCIAMACHY instrument (Gottwald et al., 2007) are used. The vertical profiles of both gases are retrieved on 1 km altitude resolution using the optimal estimation method (Rodgers, 1976).

### 3. $\text{NO}_2$ RESULTS

#### 3.1. Averaging kernels and spectral fits

The averaging kernels of the retrieval provide information on the vertical resolution and sensitivity of measurements for different altitudes. The  $\text{NO}_2$  averaging kernels shown in Fig. 1 are based on an altitude grid of 1 km.

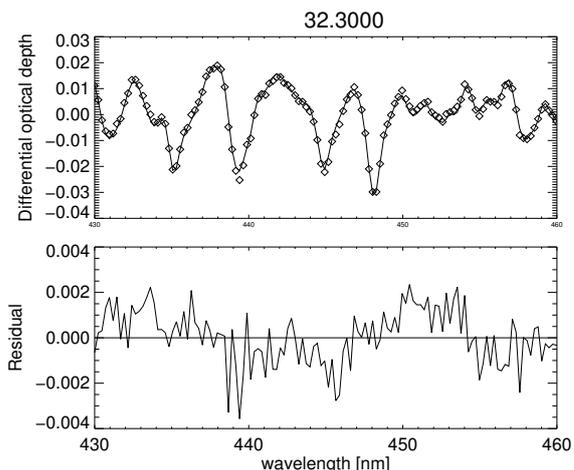


Figure 2.  $\text{NO}_2$  spectral fits and residuals at 32.3 km tangent height for orbit 10520, measurement day 05/03/2004, UTC time 01:18:53. The diamond points represent the modeled differential optical depth and the solid line the measured differential optical depth.

From the averaging kernels shown in Fig. 1, the  $\text{NO}_2$  information content in the measurement is highest between 19 and 37 km. The peaks of the averaging kernels at these altitudes are approximately 0.44–0.54. The averaging kernels at 16 km and 40 km have maximum values of 0.44 and 0.39 respectively.

Example of  $\text{NO}_2$  spectral fit and residual at tangent height of 32.3 km and covering a spectral range of 430 nm–460 nm is shown in Fig. 2. The quality of the spectral fit is good and absorption features due to  $\text{NO}_2$  are mainly seen. Below the spectral fit, is the corresponding spectral residual. The spectral residuals generally are less than 0.4 % for all relevant height layers. The systematic features seen in the spectral residual around 438–439 nm are likely to be the remaining structures of solar Fraunhofer lines of Fe (Amekudzi et al., 2007).

#### 3.2. SCIA-HALOE $\text{NO}_2$ validation results

HALOE is a solar occultation experiment on board the Upper Atmosphere Research Satellite (UARS) launched in September 1991 was operational until November 2005. The validation results of HALOE v19  $\text{NO}_2$  with  $\text{NO}_2$  from the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS), show that the agreement between HALOE v19 and ATMOS between 25 to 42 km were within 10 % and below 25 km the HALOE  $\text{NO}_2$  profiles were much lower, with larger relative differences (Randall et al., 2002). In this study we use HALOE v19 obtained from <http://haloedata.larc.nasa.gov>. The collocation criteria applied is maximum co-location radius of 1000 km and maximum measurement time difference of 12 hours between SCIAMACHY overpass and correlative HALOE measurements. Based on these criteria we found 15, 30, and 20 coincidences for 2003, 2004 and

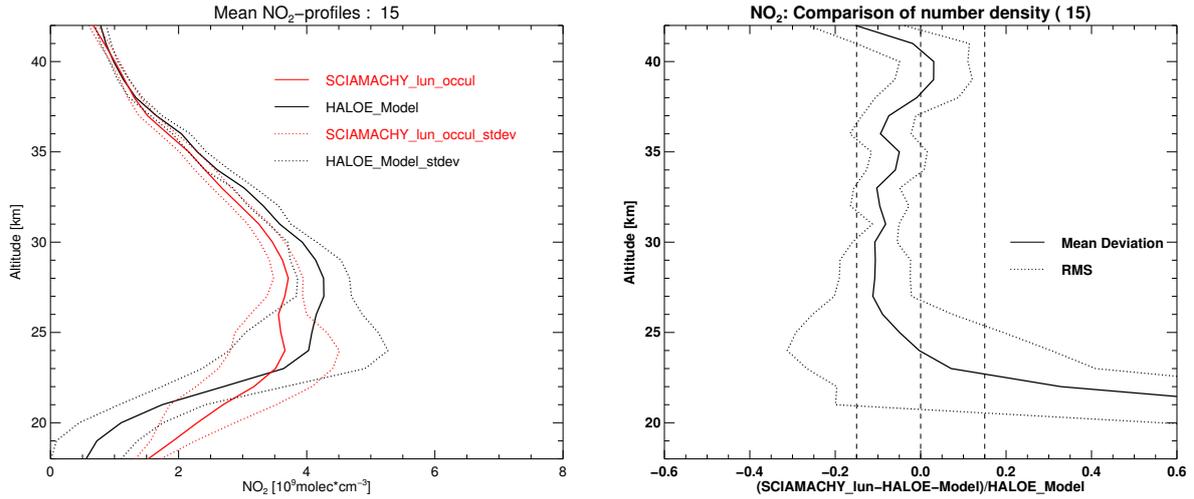


Figure 3. Left: mean  $\text{NO}_2$  density profile and corresponding standard deviation for 15 co-located events in 2003, SCIAMACHY in red and HALOE in black. Right: the relative mean deviation (solid line) and the standard deviation of the relative deviation (dotted line).

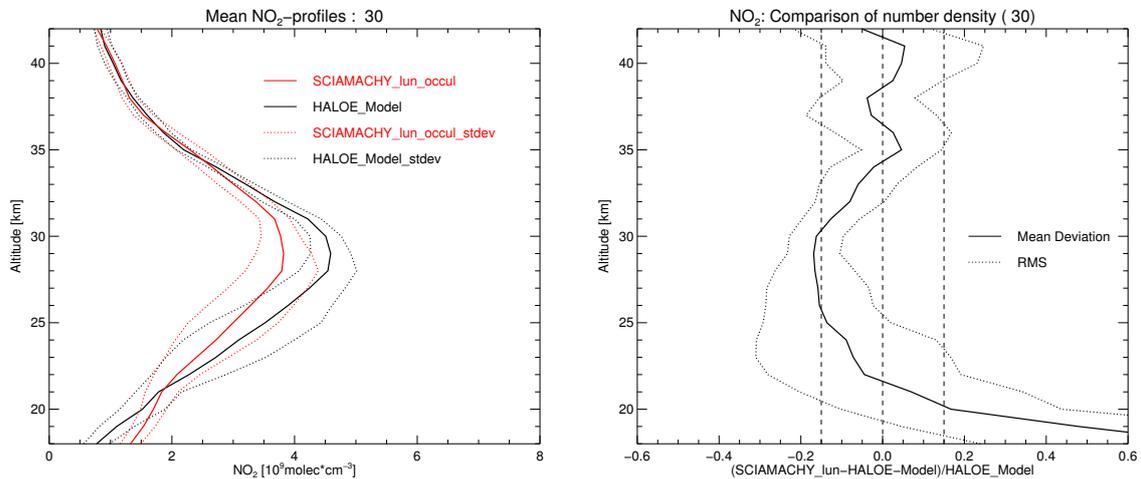


Figure 4. Left: mean  $\text{NO}_2$  density profile and corresponding standard deviation for 30 co-located events in 2004, SCIAMACHY in red and HALOE in black. Right: the relative mean deviation (solid line) and the standard deviation of the relative deviation (dotted line).

2005 respectively. A photochemical scheme described in Bracher et al. (2005) was applied to scale HALOE measurements to the SCIAMACHY lunar occultation solar zenith angles (SZA).

Figs 3, 4 and 5 show the mean, the rmd, and the rms values of SCIAMACHY comparisons with the photochemically scaled HALOE results for 2003, 2004 and 2005 respectively. In general we found good agreement with mostly negative biases. For 2003, we found that between 26–40 the rmd values are in the range of -13 % to +2 %. The standard deviations in the same altitudes are within 3 % to 15 %. In Fig. 4 (right), we found that the rmd and rms values for 2004 comparisons are within -16 % to +5 % and 6–19 % respectively between 25–42 km. The

rmd and rms values for 2005 comparisons are between -23 % to +3 % and 4 % to 16 % respectively. The observed biases are likely due to the uncertainties in the photochemical model scheme, which is about 14 % (Bracher et al., 2005).

### 3.3. SCIA-SAGE II $\text{NO}_2$ validation results

SAGE II was launched on the Earth Radiation Budget Satellite (ERBS) in October 1984 was in operation until August 2005. The  $\text{NO}_2$  data quality of SAGE II v5.96 according to Cunnold et al. (1991) are within 10 % between 23 and 37 km. In this study the  $\text{NO}_2$  data version 6.2

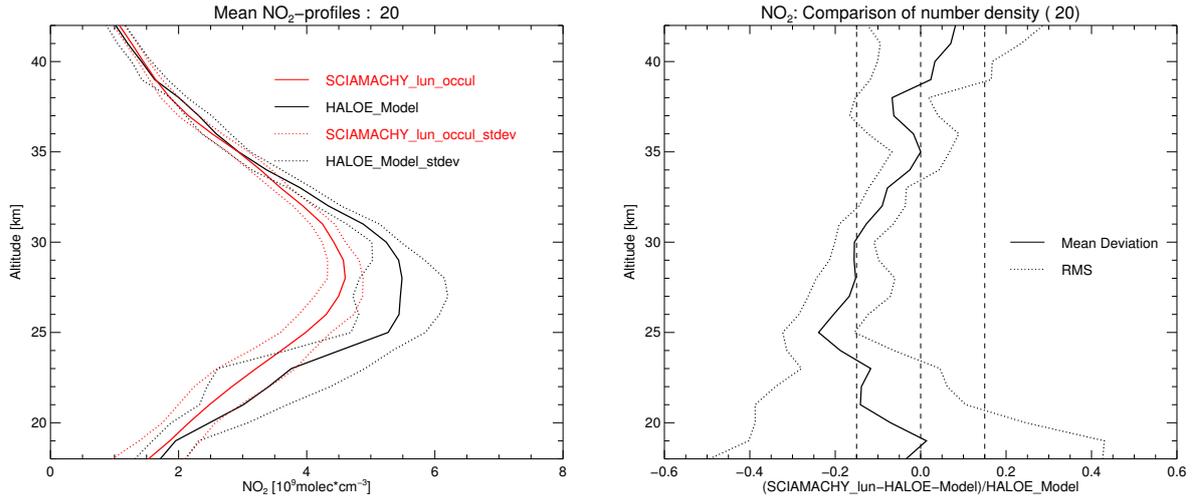


Figure 5. Left: mean  $\text{NO}_2$  density profile and corresponding standard deviation for 20 co-located events in 2005, SCIAMACHY version 2.2 in red and HALOE in black. Right: the relative mean deviation (solid line) and the standard deviation of the relative deviation (dotted line).

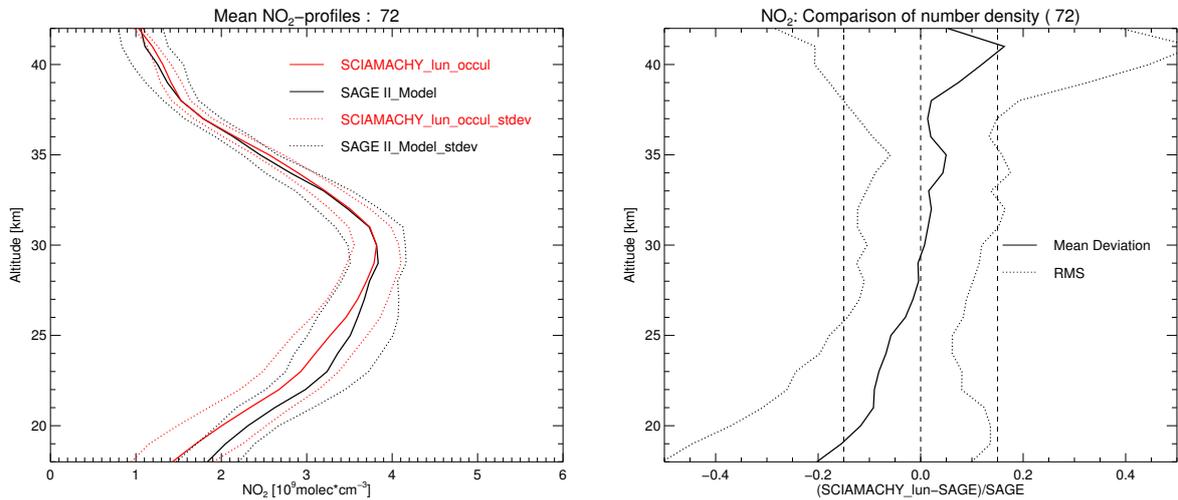


Figure 6. Left: mean  $\text{NO}_2$  density profile and corresponding standard deviation for 72 co-located events in 2004, SCIAMACHY in red and SAGE II in black. Right: the relative mean deviation (solid line) and the standard deviation of the relative deviation (dotted line).

obtained from <http://www.sage2.larc.nasa.gov/data> is used. The co-location criteria applied is the same as that for SCIA-HALOE validation. We found 72 co-locations for 2004 and no coincidences are found in 2003 and 2005. Like SCIA-HALOE validation, SAGE II  $\text{NO}_2$  results are photochemically scaled to SCIAMACHY SZA and the scaled results compared to SCIAMACHY  $\text{NO}_2$  profiles. The statistical results of these comparisons are shown in Fig. 6. Very good agreement in the mean profiles between 26 and 38 km are observed. Below 27 km the scaled SAGE II profiles are slightly higher than SCIAMACHY version 2.2 results. Negative biases are seen in the altitude range of 20–29 km with rmd values within -11 % to -0.4 %. Between 30 to 42 km positive biases are observed

with rmd values in the range of +0.7 % to +16 %. The rms values are in the range of 10 % to 14 % between 24 and 37 km.

## 4. $\text{NO}_3$ RESULTS

### 4.1. $\text{NO}_3$ averaging kernels and spectral fit

Averaging kernels for  $\text{NO}_3$  retrieval altitudes between 16 and 55 km is displayed in Fig. 7. From the averaging kernels, the highest sensitivity of  $\text{NO}_3$  is about 0.7 at 35 km. Followed by the sensitivity at 21 and 30 km, which is

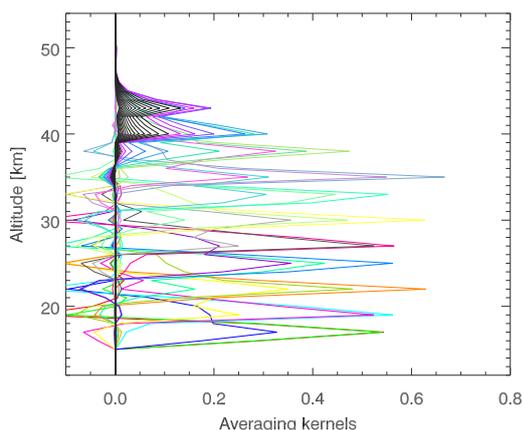


Figure 7.  $\text{NO}_3$  averaging kernels for the retrieval altitude 16–55 km for orbit 09699, measurement day 07/01/2004, UTC time 16:48:23.

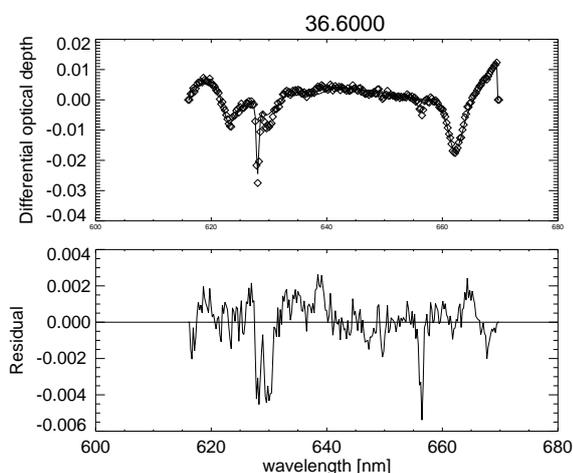


Figure 8.  $\text{NO}_3$  spectral fits and residuals at 36.6 km tangent height for orbit 09699, measurement day 07/01/2004, UTC time 16:48:23. The diamond points represent the modeled differential optical depth and the solid line the measured differential optical depth.

about 0.6. The sensitivities between 16 to 20 km and 22 to 30 km are about 0.55. The lowest sensitivity is about 0.2 at 45 km.

Fig. 8 shows an example of the spectral fit (top) and residual (bottom) at 36.6 km tangent height. The quality of the fit is good and the absorption features of  $\text{NO}_3$  at 623 nm and 662 nm are accurately fitted. The residuals are less than 0.2 % in most parts of the selected spectral window (615–670 nm). A systematic features seen around 656–657 nm in the spectral residuals are likely to be the remaining structures of solar Fraunhofer lines of  $\text{H}_\alpha$ . Whereas the systematic features seen around 627–630 nm are likely to be the remaining structures of  $\text{O}_2$ -A.

## 4.2. $\text{NO}_3$ inter-comparisons results

Based on our previous studies in Amekudzi et al. (2005b), we carried out the inter-comparisons between our current retrieval results (SCIAMACHY version 2.2) with the previous results (SCIAMACHY version 2.1) and the results of the simple model calculations. The simple model scheme is described in Amekudzi et al. (2005b). The simple model scheme assumed that the thermal decomposition of  $\text{N}_2\text{O}_5$  to form  $\text{NO}_3$  and  $\text{NO}_2$  is negligible at steady state.

Fig. 9 shows examples of the inter-comparison of retrieved  $\text{NO}_3$  results with model. In general the model results are in better agreement with the version 2.2 products. From all the comparisons, we see larger differences between the version 2.1 and version 2.2 below 23 km, these are likely due to differences in the true measurement information retrieved. The measurement altitude sampling information for the version 2.2 products are between 16 and 55 km, and for the version 2.1 product are between 22–55 km. The two versions results and the model are however in good agreement between 24 and 38 km.  $\text{NO}_3$  concentrations in the stratosphere are strongly temperature dependent, the different temperature profiles used in the two retrievals scheme could likely explain the observed differences between the version 2.1 and 2.2 above 35 km for the results in March.

## 5. SUMMARY AND CONCLUSIONS

In this paper, we report on the current retrieval results of nighttime  $\text{NO}_x$  ( $\text{NO}_2$  and  $\text{NO}_3$ ) from SCIAMACHY lunar occultation measurements.

We demonstrate that high quality spectral fits showing absorption features of  $\text{NO}_2$  and  $\text{NO}_3$  are obtained with reasonable spectral residuals in the range of 0.1–0.5 %. The averaging kernels showing information content of  $\text{NO}_2$  and  $\text{NO}_3$  retrieval are shown, where we demonstrated that the  $\text{NO}_2$  and  $\text{NO}_3$  can be retrieved with our retrieval code between 16–42 km and 16–45 km respectively.

We compared the SCIAMACHY nighttime  $\text{NO}_2$  (version 2.2) with co-located photochemically scaled HALOE and SAGE II  $\text{NO}_2$  profiles and obtained promising results. In general we obtain negative biases for SCIAMACHY-HALOE validation with rmd and rms within -16 % to +3 % and 4–16 % respectively. For SCIAMACHY-SAGE II validation, negative biases are observed between 20–29 km and above 29 km positive biases are seen. The rmd and rms are within -9 % to +7 % and 10–17 % between 22–39 km.

$\text{NO}_3$  profiles version 2.2 are compared with simple model and the previous (version 2.1) results. In general better results are obtained for version 2.2 comparisons with model between 16 and 38 km within accuracy of 25 %. The observed differences above 35 km between version

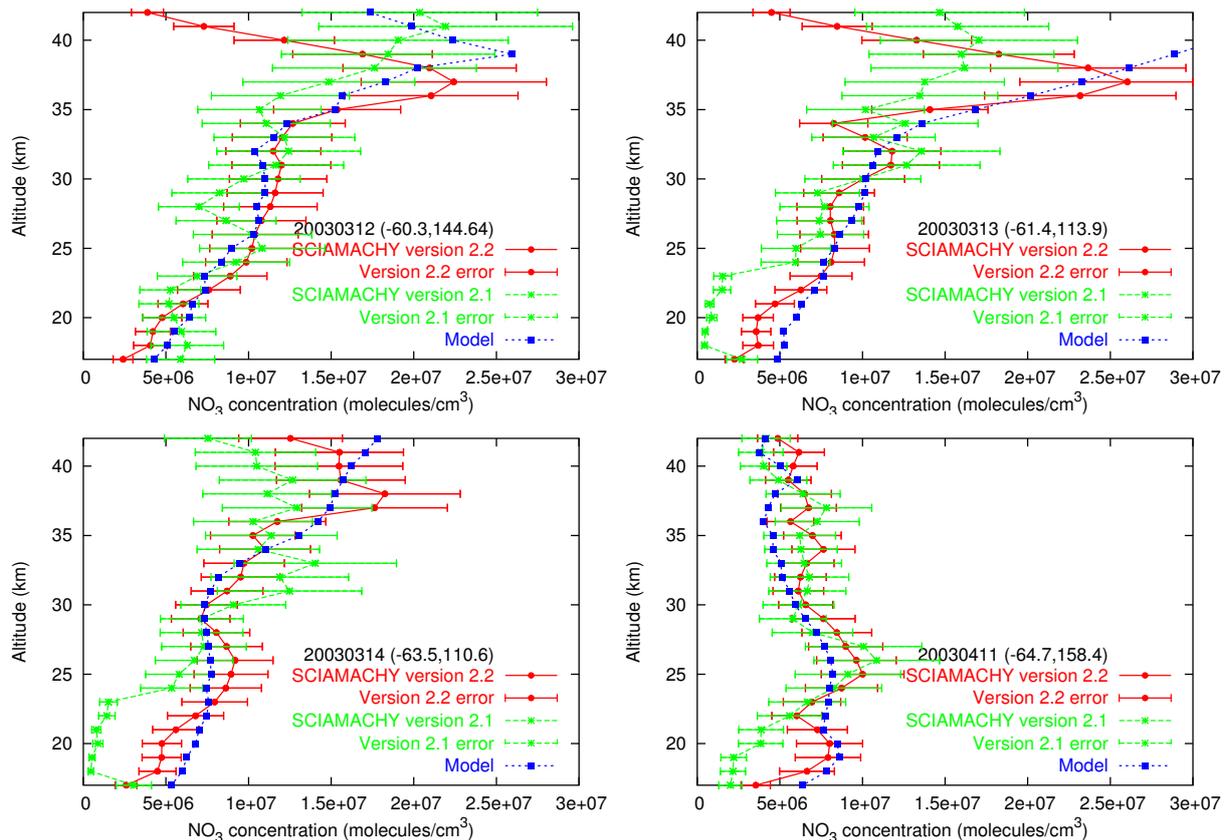


Figure 9. Example of  $\text{NO}_3$  vertical profiles inter-comparison results for March 12, 13, 14, and April 12, 2003 at SZA of  $105^\circ$ ,  $109^\circ$ ,  $111^\circ$ , and  $115^\circ$  respectively. SCIAMACHY version 2.1 in green, version 2.2 in red and simple model results in blue. The red and green error bars are the maximum retrieval errors of 25% and 35% of the versions 2.2 and 2.1 results respectively.

2.1 and 2.2 are likely due to different temperature information used.

Further validation with other instruments and a comprehensive 1-D photochemistry model, will confirm the quality of the SCIAMACHY version 2.2 nighttime  $\text{NO}_x$  products. A comparison with SAGE III lunar occultation products is planned for the future. Complete processing and extensive validation of SCIAMACHY lunar occultation data set will provide a long term useful nighttime  $\text{NO}_x$  data base for scientific analysis and validation of other instruments.

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