

NIGHTTIME NO_X FROM SCIAMACHY LUNAR OCCULTATION MEASUREMENTS

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Abstract

Vertical profiles of stratospheric NO₂ and NO₃ have been retrieved from moderately resolution atmospheric lunar transmission spectra measured by SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) on board the ENVISAT (Environmental Satellite). The measurements were taken over the high Southern latitude (50° S–90° S). The global spectra fitting method by differential optical depth approach were used to fit NO₂ and NO₃ using the spectral window of 430–460 nm and 615–680 nm respectively. To assess the accuracy of the retrieved NO₂ profiles the SCIAMACHY nighttime NO₂ profiles were compared with daytime NO₂ profiles measured by Halogen Occultation Experiment (HALOE), using photochemical correction model. The validation results show that the quality of SCIAMACHY nighttime NO₂ is high within 5–20% in the altitude range of 24–39 km. Our current understanding of NO₃ chemistry and the internal consistency of the retrieved NO₃ profiles were verified with a complex and a relatively simple model scheme. The complex model uses a comprehensive photochemistry of the stratosphere and the simple model uses only SCIAMACHY ozone and ECMWF temperature and pressure analyses as input. We found that the retrieved NO₃ profiles are in very good agreement with the model calculations within the expected accuracy of 20–35 %.

1. INTRODUCTION

The recognition of the importance of nitrogen species in the Antarctic ozone depletion process have led to increase in observations of NO, NO₂, NO₃, N₂O₅, and HNO₃ in the polar regions [(Solomon, 1990) and references therein]. Nighttime NO_X is mainly NO₂ and NO₃ as NO is rapidly oxidized by the surrounding ozone molecules to NO₂ and NO₂ is further oxidized by ozone to NO₃. NO₂ and NO₃ thus are key molecules involved in nighttime ozone chemistry in the stratosphere. To completely assess the contribution of NO_X to long-term ozone loss process in the stratosphere, it is important to measure simultaneously NO₂ and NO₃.

One excellent way to measure the nighttime concentration of NO₂ and NO₃ is by the lunar occultation measurement technique. This method has been applied successfully by ground based platforms (Noxon *et al.*, 1978; Platt *et al.*, 1981; Sander *et al.*, 1987; Solomon *et al.*, 1989, 1993) and balloon platforms (Naudet *et al.*, 1981, 1989; Renard *et al.*, 1996, 2001). Lunar occultation measurement technique has recently been introduced on satellite platforms. The space-borne instruments applying this measurement technique are the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography on the ENVISAT platform launched in March 2002 and the third Stratospheric Aerosol and Gas Experiment on the meteor-3M launched in December 2001.

The focus of this paper is to report on the retrieved vertical profiles of NO₂ and NO₃ from SCIAMACHY lunar occultation measurements. The retrieved NO₂ validation results will be presented in Section 2. In Section 3, we will present comparisons of retrieved NO₃ with model result. The diurnal variability observed in the retrieved data will be discussed in Section 4. Finally the conclusions to our study will be presented in Section 5.

2. VALIDATION OF NO₂

In this section, we present the validation results of NO₂ vertical profiles retrieved from SCIAMACHY lunar occultation level-1 data. The retrieval method have been described in Amekudzi (2005). The global spectra fitting method by differential optical depth approach was used to simultaneously fit NO₂ and O₃ using the spectral window of 430–460 nm and 520–580 nm. Furthermore, NO₂ and O₃ profiles were jointly retrieved using the optimal estimation method described in Rodgers (1976, 2000). Preliminary validation of SCIAMACHY lunar NO₂ have been reported in Amekudzi *et al.* (2005a), where SCIAMACHY lunar NO₂ were compared to MIPAS and SAGE III NO₂ results. In this study no photochemical correction scheme procedure was applied, because only measurements at similar SZAs were compared.

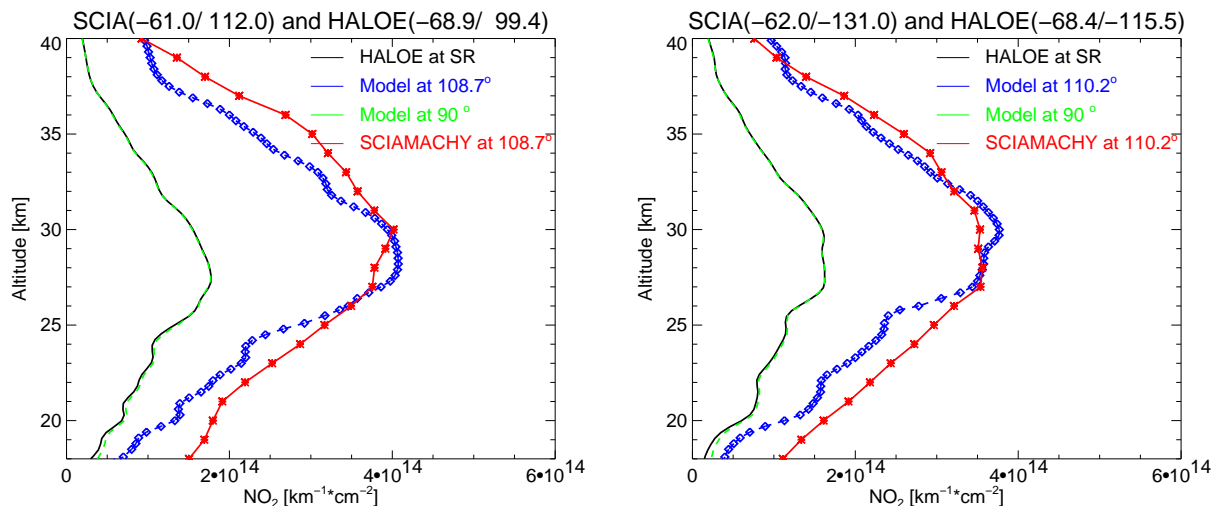


Figure 1. Examples of NO₂ density profiles for SCIAMACHY compared with HALOE. The red line is the SCIAMACHY result and blue HALOE photochemically corrected to SCIAMACHY SZA. The black line is HALOE NO₂ profile and the green line the model at HALOE SZA. Left: result for SCIAMACHY SZA of 108.7 and right: result for SCIAMACHY SZA of 110.2.

The concentration of NO₂ depends strongly on the local-time and the history of exposure to sunlight (Solomon *et al.*, 1993), which makes validation of NO₂ measurements difficult. In particular as SCIAMACHY in lunar occultation mode starts measurements a few hours (1–3 hrs) after sunset and a few hours before sunrise, it is more difficult to get coincident measurements both in location and SZA. To carry out validation study for retrieved NO₂ profiles from SCIAMACHY lunar occultation at Solar Zenith Angle (SZA) $\geq 95^\circ$ with retrieved NO₂ profiles from HALOE solar occultation measurement at SZA ≤ 90 , it is important to use a photochemical model to transform the HALOE measurements at SZA ≤ 90 to those predicted for the SZA of SCIAMACHY lunar occultation measurements. The photochemical model used is described in Bracher *et al.* (2005); this model is similar to the SLIMCAT photochemical model (Chipperfield, 1999; Sinnhuber *et al.*, 2003). The model includes 135 chemical reactions including gas-phase and heterogeneous reactions, 44 photolysis reactions of 52 species, which are of relevance to stratospheric chemistry. The model was run with a chemical time-step of 5 min and model output is every 15 min. The photochemical scheme in the 1-D model was driven from the chemistry scheme of the 2-D model, and considers exactly the same chemical reactions and species. The model is run over a period of 3 days. NO₂ profiles from HALOE sunrise measurements are transformed to the SZA of the SCIAMACHY lunar occultation measurement, then these two NO₂ results are compared.

The HALOE NO₂ data version 19 (v19) downloaded from (<http://haloedata.larc.nasa.gov>) was used for this study. The accuracy of the HALOE NO₂ v19 are within 10–15% from altitude range of 20–40 km in clear air conditions, but exhibit a low bias in the presence of aerosols loading (Gordley *et al.*, 1996). The vertical resolution of HALOE data is around 2 km. The spatial criteria applied was based on collocated radius in the range of 600–1000 km. Based on this criteria we found 15 coincident measurements.

NO₂ example profiles are shown in Figure 1. The results of the mean profiles, the relative mean deviations and the standard deviations of the 15 coincident measurements are shown in Figure 2. In general we found good agreement between the SCIAMACHY and HALOE photochemically corrected to SCIAMACHY SZA between 24–39 km with the relative deviations in the range of -13% to +20%. The standard deviations in the same altitude range are between 5–20%. However large biases are observed below 24 km. These differences are probably due to uncertainties in the input parameters of the photochemical model used. The photochemical model input parameters errors include inaccuracies in the photolysis frequencies of the photochemical reactions and reaction rates, the initialized NO_x and O₃ from measurement, temperature, and aerosol loading of the atmosphere. An estimate of the model input parameter errors is less than 14% in the altitude range of 15–40 km (Bracher *et al.*, 2005).

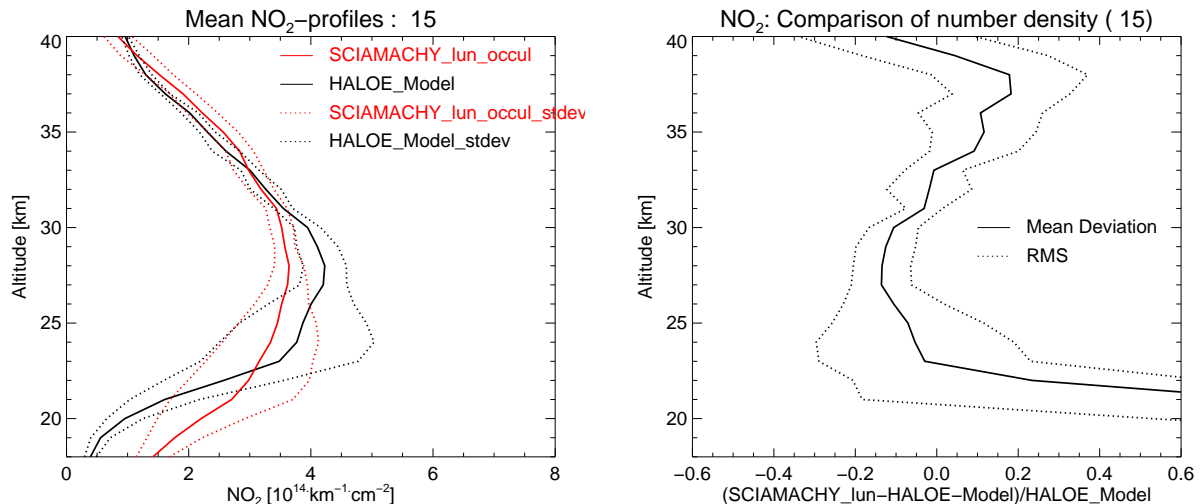


Figure 2. Left: mean NO₂ density profile for 15 collocated events, SCIAMACHY result in red and HALOE photochemically corrected to SCIAMACHY SZA in black. Right: the mean relative deviation in solid line and the standard deviation in dotted lines.

3. NO₃ RETRIEVAL AND COMPARISON WITH MODEL

Here, the results of NO₃ vertical profiles retrieved from the SCIAMACHY lunar occultation spectra and comparisons of retrieved profiles with model are presented. The nitrate radical, NO₃, has two strong absorption peaks, i.e. absorption band at 623 and 662 nm. We utilized both absorption bands to retrieve number density profile of NO₃. The absorption bands near 623 nm and 662 nm, however have significant contributions from other absorbers such as O₃, O₂, O₄, and H₂O. To accurately fit and retrieve NO₃ profiles, these strong absorbers were fitted in addition to NO₃. As O₂ and H₂O are line absorber, their absolute cross sections were calculated using line-by-line spectral simulation code. Broadband absorption features of the atmosphere and instrument from the measured spectrum were removed by subtracting a third order polynomial. Details of the NO₃ retrieval method and comparisons with model have been reported in Amekudzi *et al.* (2005b).

3.1 NO₃ retrieval results

Figure 3 (left) shows an example of the spectral fit at 39 km tangent height for March 12, 2003, corresponding to ENVISAT orbit 5390 and SZA of 105.8°. The dotted line is the modeled differential optical depth and the solid line represents the measured differential optical depth. The quality of the fit is good, as the absorption band of NO₃ near 623 nm and 662 nm are accurately fitted. The spectral residual (not shown) is in the order of 0.2% for all relevant height layers (Amekudzi, 2005).

The zonal mean profiles of NO₃ concentration retrieved from SCIAMACHY lunar occultation measurements between March and June 2003 shown in Figure 3 (right) indicates higher concentration of retrieved NO₃ in the moderately high latitudes (60° S–65° S). These high values were mainly due to the contribution from warmer days. The measurement data corresponding to 60° S–65° S were taken in March where the stratosphere was relatively warm. The low values of retrieved NO₃ were observed in the high latitude (70° S–85° S). These values are mainly the contribution from measurements in April, May, and June where the temperature in the stratosphere was relatively low.

3.2 Comparisons of retrieved NO₃ with model

In order to verify our understanding of the NO₃ nighttime chemistry and the internal consistency of the observations, the retrieved NO₃ profiles were compared with model calculations. Two model schemes were used, a complex model and a relatively simple model. The complex model scheme uses a comprehensive photochemistry of the stratosphere and the simple model scheme uses only SCIAMACHY lunar occultation retrieved ozone (Amekudzi *et al.*, 2005a) and ECMWF temperature and pressure analyses as input. The complex model scheme is similar to the photochemical correction scheme discussed in Section 2, details of this model are given in [Sinnhuber *et al.* (2003) and references therein]. The complex model scheme used was constrained by temperature and pressure profiles from ECMWF analyses and ozone and NO₂ profiles from SCIAMACHY observations.

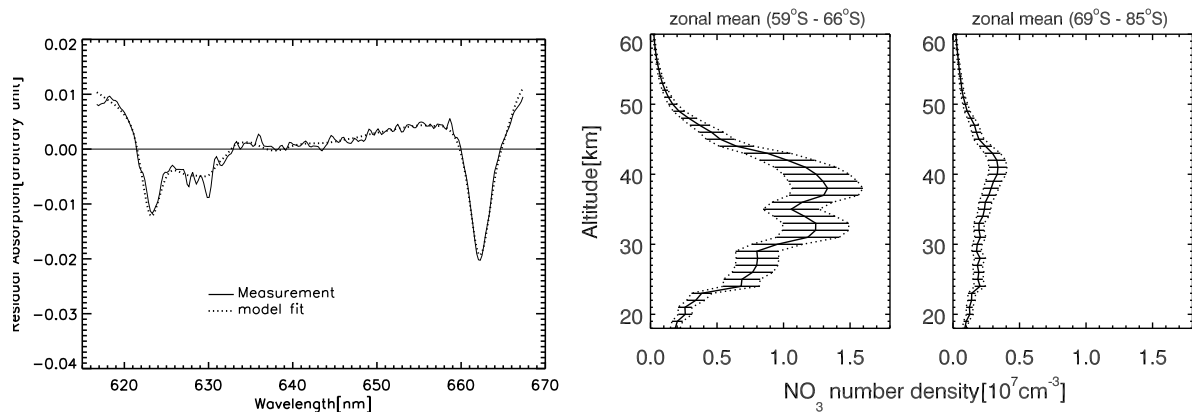


Figure 3. Left: the fit at 39 km tangent height for March 12, 2003, orbit number 5390, and SZA 105.8° . Right: the zonal mean profiles of NO_3 retrieved from SCIAMACHY lunar occultation for latitude band of 60°S – 65°S and 70°S – 85°S . The shaded region show the maximum possible error of 35%. The analysis is based on 35 profiles for 60°S – 65°S and 95 profiles for 70°S – 85°S .

NO_2 was constrained by scaling the modeled NO_y (in particular NO , NO_2 , N_2O_5 , and HNO_3) until the modeled NO_2 agrees with measured NO_2 at the time of the SCIAMACHY measurements (Amekudzi *et al.*, 2005b). The relatively simple model assumed that at steady state the nighttime concentration of NO_3 depend on the concentration of O_3 and temperature.

Figure 4 (left) shows the comparison of retrieved NO_3 with calculated NO_3 from the complex and simple models for 12 April 2003. In general we found very good agreement between retrieved and complex model calculated NO_3 within the expected error of 35% between the altitude range of 24–45 km and with the simple model up to 35–40 km. We verified the consistency in the retrieved NO_3 profiles by plotting the retrieved NO_3 as a function of simple model calculated NO_3 . Contribution of NO_3 concentrations above 40 km were removed from this study. Example of this result is shown in Figure 4 (right). We found very good correlation between the retrieved and the simple calculated model with correlation coefficient in the range of 0.83–0.98 (Amekudzi, 2005).

4. DIURNAL VARIABILITY OF NIGHTTIME NO_x

NO_2 and NO_3 exhibit strong diurnal variation, during daytime atmospheric NO_x is mainly in form of NO and NO_2 , as NO_3 is rapidly photolyzed. The daytime stratospheric NO concentration is however far more than the concentration of NO_2 . Just after sunset, the stratospheric NO is rapidly oxidized to NO_2 by O_3 and NO_2 is further oxidized by O_3 to NO_3 . The concentration of both NO_2 and NO_3 thus build up few minutes after sunset, the limiting factors being complete removal of NO , temperature and the reaction of NO_2 and NO_3 in the presence of collision partner to form N_2O_5 . We observed the diurnal variation in nighttime NO_2 and NO_3 retrieved concentrations from SCIAMACHY lunar occultation spectra. These results are displayed in Figure 5.

5. CONCLUSIONS

The retrieved vertical profiles of nighttime NO_x ($\text{NO}_2 + \text{NO}_3$) over high latitudes in the Southern hemisphere have been presented. The quality of our retrieved NO_2 profiles were verified, by comparing with photochemically corrected HALOE NO_2 profiles. We found good agreement with standard deviations of 5–20%.

Our current understanding of stratospheric NO_3 chemistry at the location of measurements have been verified with model. We found good agreement with model within the expected accuracy of 20–35%, demonstrating that we have reasonable understanding of NO_3 chemistry in the polar stratosphere. Furthermore the internal consistency was check with the simple model. We found very good correlation with correlation coefficient in the range of 0.83–0.98.

We observed that the retrieved NO_2 and NO_3 show strong diurnal variation. A study on the diurnal variation will be carried out in the future. In addition, further validation study on SCIAMACHY nighttime NO_2 will also be carried out in the future.

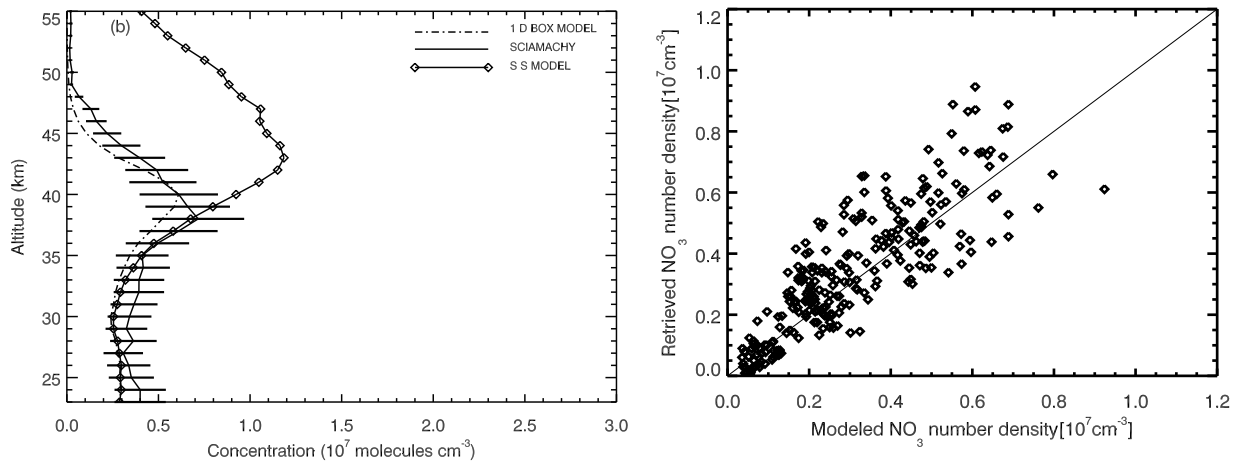


Figure 4. Left: example of retrieved NO_3 profiles compared with model results for 12th of April, 2003 at SZA of 115° . Solid line is the retrieval result, the dashed-dotted line is the complex model output and the solid line with diamond points the simple. Right: retrieved NO_3 as a function of the simple model calculated NO_3 for latitude band of $66\text{--}72^\circ$ S. The correlation coefficient for this graph is 0.98.

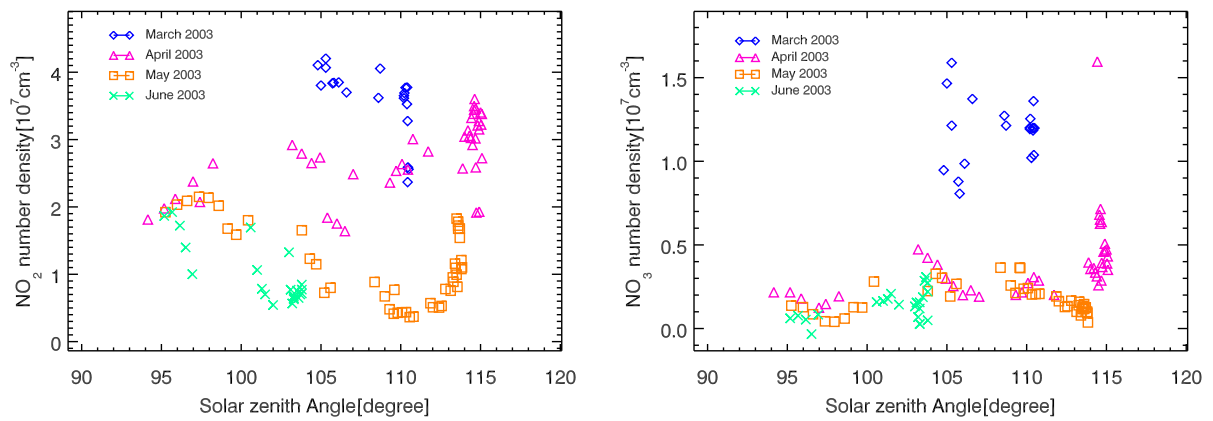


Figure 5. Solar zenith angle dependence of NO_2 and NO_3 for 2003 SCIAMACHY lunar occultation measurements, NO_2 result at 30 km (left) and NO_3 result at 40 km (right).

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