NIGHTTIME NO_X FROM SCIAMACHY LUNAR OCCULTATION MEASUREMENTS

L. K. Amekudzi, A. Bracher, K. Bramstedt, H. Bovensmann, and J. P Burrows

Abstract

Vertical profiles of stratospheric NO_2 and NO_3 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^o S–90^o S). The global spectra fitting method by differential optical depth approach were used to fit NO_2 and NO_3 using the spectral window of 430–460 nm and 615–680 nm respectively. To assess the accuracy of the retrieved NO_2 profiles the SCIAMACHY nighttime NO_2 profiles were compared with daytime NO_2 profiles measured by Halogen Occultation Experiment (HALOE), using photochemical correction model. The validation results show that the quality of SCIAMACHY nighttime NO_2 is high within 5–20% in the altitude range of 24–39 km. Our current understanding of NO_3 chemistry and the internal consistency of the retrieved NO_3 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 NO_3 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, NO_2, NO_3, N_2O_5, and HNO_3 in the polar regions [(*Solomon*, 1990) and references therein]. Nighttime NO_X is mainly NO_2 and NO_3 as NO is rapidly oxidized by the surrounding ozone molecules to NO_2 and NO_2 is further oxidized by ozone to NO_3. NO_2 and NO_3 thus are key molecules involved in nighttime ozone chemistry in the stratosphere. To completely asses the contribution of NO_X to long-term ozone loss process in the stratosphere, it is important to measure simultaneously NO_2 and NO_3.

One excellent way to measure the nighttime concentration of NO_2 and NO_3 is by the lunar occultation measurement technique. This method has been applied successful 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 NO_2 and NO_3 from SCIAMACHY lunar occultation measurements. The retrieved NO_2 validation results will be presented in Section 2. In Section 3, we will present comparisons of retrieved NO_3 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 NO_2

In this section, we present the validation results of NO_2 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 NO_2 and O_3 using the spectral window of 430–460 nm and 520–580 nm. Furthermore, NO_2 and O_3 profiles were jointly retrieved using the optimal estimation method described in *Rodgers* (1976, 2000). Preliminary validation of SCIAMACHY lunar NO_2 have been reported in *Amekudzi et al.* (2005a), where SCIAMACHY lunar NO_2 were compared to MIPAS and SAGE III NO_2 results. In this study no photochemical correction scheme procedure was applied, because only measurements at similar SZAs were compared.

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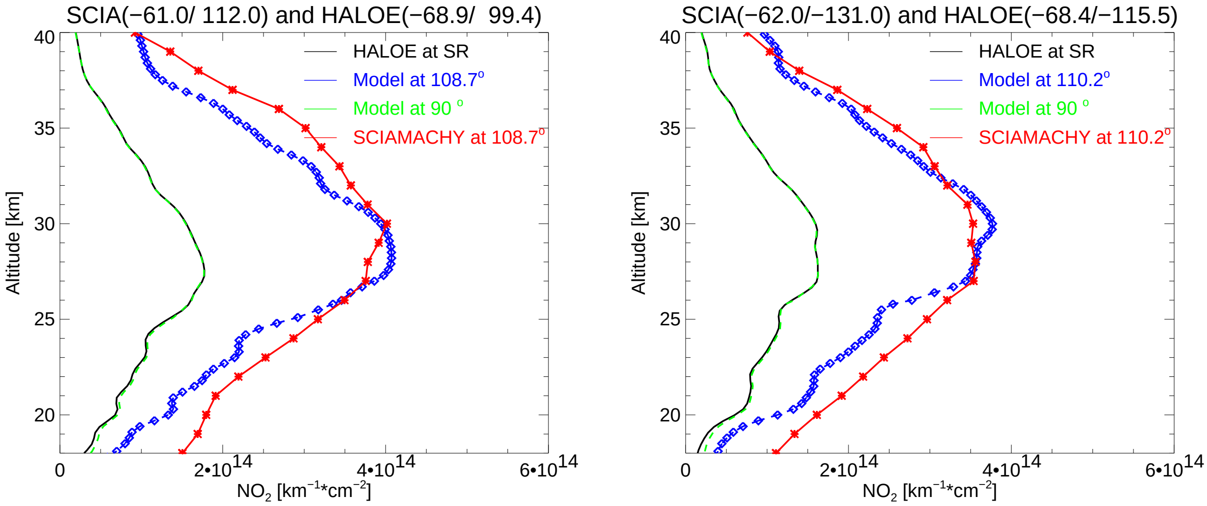

Figure 1. Examples of NO_2 density profiles for SCIAMACHY compared with HALOE. The red line is the SCIAMACHY result and blue HALOE photochemically corrected to SCIAMACHY SZA. The black line is HALOE NO_2 profile and the green line the model at HALOE SZA. Left: result for SCIAMACHY SZA of 108.7 and right: result for SCIAMACHY SZA of 110.2.

The concentration of NO_2 depends strongly on the local-time and the history of exposure to sunlight (*Solomon et al.*, 1993), which makes validation of NO_2 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 NO_2 profiles from SCIAMACHY lunar occultation at Solar Zenith Angle (SZA) $\geq 95°$ with retrieved NO_2 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. NO_2 profiles from HALOE sunrise measurements are transformed to the SZA of the SCIAMACHY lunar occultation measurement, then these two NO_2 results are compared.

The HALOE NO_2 data version 19 (v19) downloaded from (http://haloedata.larc.nasa.gov) was used for this study. The accuracy of the HALOE NO_2 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.

NO_2 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 O_3 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).

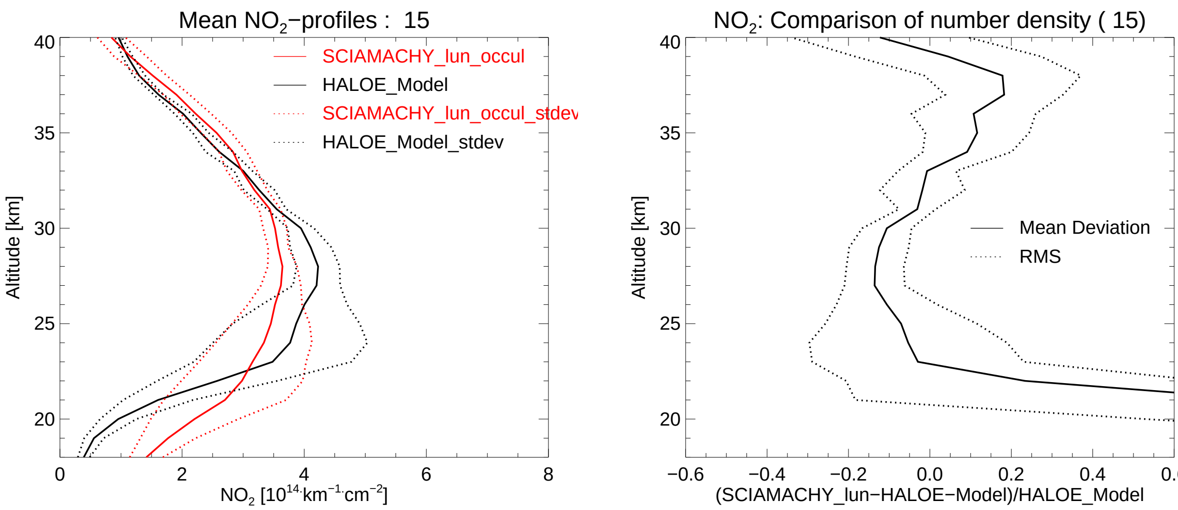

Figure 2. Left: mean NO_2 density profile for 15 collocated events, SCIAMACHY result in red and HALOE photochemically corrected to SCIAMACHY SZA in black. Right: the mean relative deviation in solid line and the standard deviation in dotted lines.

3. NO_3 RETRIEVAL AND COMPARISON WITH MODEL

Here, the results of NO_3 vertical profiles retrieved from the SCIAMACHY lunar occultation spectra and comparisons of retrieved profiles with model are presented. The nitrate radical, NO_3, 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 NO_3. The absorption bands near 623 nm and 662 nm, however have significant contributions from other absorbers such as O_3, O_2, O_4, and H_2O. To accurately fit and retrieve NO_3 profiles, these strong absorbers were fitted in addition to NO_3. As O_2 and H_2O 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 NO_3 retrieval method and comparisons with model have been reported in *Amekudzi et al.* (2005b).

3.1 NO_3 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 NO_3 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 NO_3 concentration retrieved from SCIAMACHY lunar occultation measurements between March and June 2003 shown in Figure 3 (right) indicates higher concentration of retrieved NO_3 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 NO_3 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 NO_3 with model

In order to verify our understanding of the NO_3 nighttime chemistry and the internal consistency of the observations, the retrieved NO_3 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 NO_2 profiles from SCIAMACHY observations.

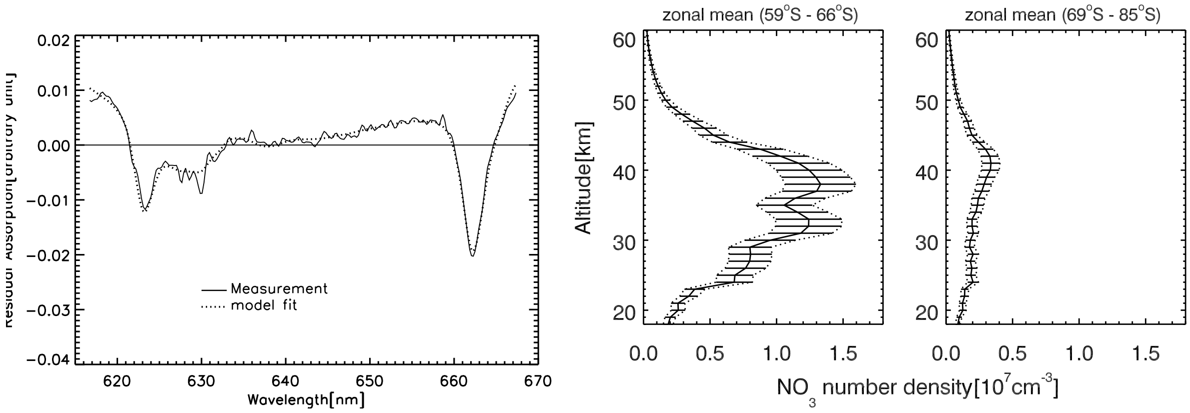

Figure 3. Left: the fit at 39 km tangent height for March 12, 2003, orbit number 5390, and SZA 105.8°. Right: the zonal mean profiles of NO_3 retrieved from SCIAMACHY lunar occultation for latitude band of 60° S–65° S and 70° S–85° S. The shaded region show the maximum possible error of 35%. The analysis 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 (NO_2 + 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.

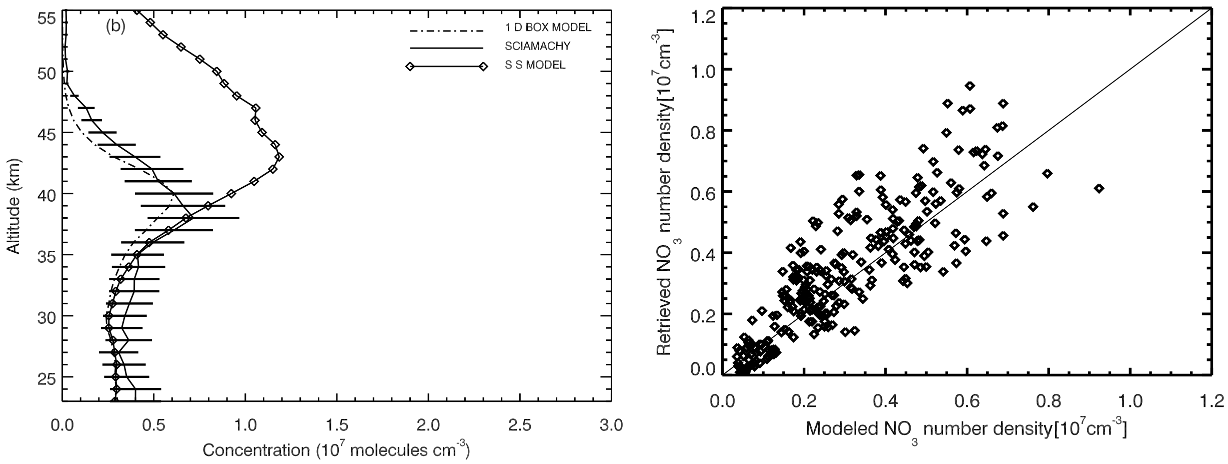

Figure 4. Left: example of retrieved NO_3 profiles compared with model results for 12th of April, 2003 at SZA of 115°. Solid line is the retrieval result, the dashed-dotted line is the complex model output and the solid line with diamond points the simple. Right: retrieved NO_3 as a function of the simple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

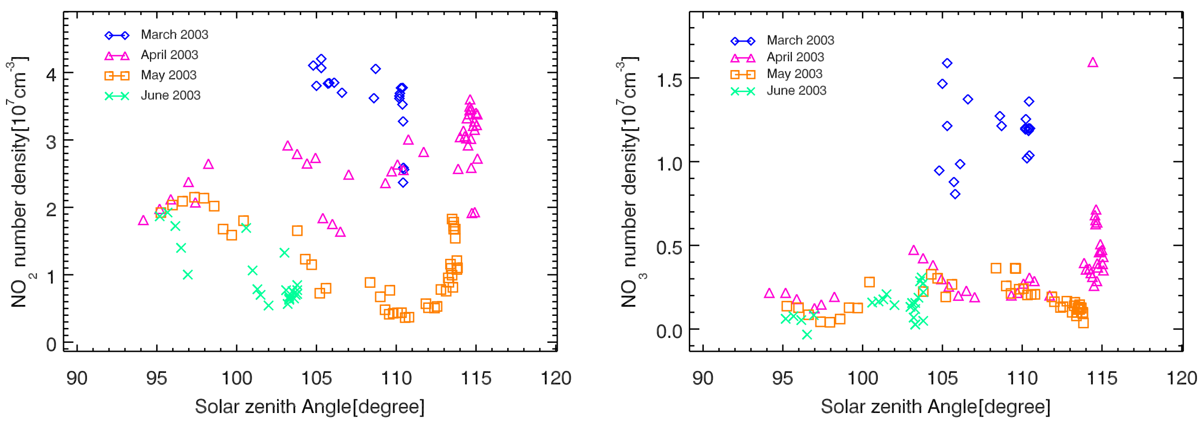

Figure 5. Solar zenith angle dependence of NO_2 and NO_3 for 2003 SCIAMACHY lunar occultation measurements, NO_2 result at 30 km (left) and NO_3 result at 40 km (right).

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