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Validation of the self-consistency of GOMOS NO_3, NO_2 and O_3 data using chemical data assimilation

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[1] The NO_3 measurement by the GOMOS instrument on board the ENVISAT platform is the first satellite measurements of this species. The simultaneous measurements of O_3 and NO_2, which are strongly coupled chemically to NO_3, allow us to test the self-consistency of the GOMOS measurements of the different species. In this paper, the self-consistency of the nighttime measurements by GOMOS of O_3, NO_2 and NO_3 are tested using chemical data assimilation. Measurements obtained between 25 and 55 km during two distinct periods are assimilated. Analyzed NO_3 (i.e., NO_3 calculated by the model after assimilation of GOMOS O_3 and NO_2 data) are then compared to corresponding GOMOS NO_3 measurements in correlation plots (GOMOS NO_3 versus analyzed NO_3). Overall, the differences between the NO_3 measurements and corresponding analyzed NO_3 are found to be small, about 10% on average. The linear regressions for both periods are also found to be close to the 1-to-1 line with small standard errors. This agreement indicates that O_3, NO_2 and NO_3 GOMOS measurements are self consistent chemically and that there is no substantial bias in GOMOS NO_3 data. It also suggests that the nighttime NO_3 chemistry is well understood. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 3210 Mathematical Geophysics: Modeling; 3337 Meteorology and Atmospheric Dynamics: Numerical modeling and data assimilation. **Citation:** Marchand, M., S. Bekki, A. Hauchecorne, and J.-L. Bertaux (2004), Validation of the self-consistency of GOMOS NO_3, NO_2 and O_3 data using chemical data assimilation, *Geophys. Res. Lett.*, *31*, L10107, doi:10.1029/2004GL019631.

1. Introduction

[2] Nitrogen oxides (NO_x = NO + NO_2) are of primary importance in controlling stratospheric ozone levels. In the middle stratosphere, reactions involving NO_x form the primary catalytic O_3 destruction cycle. In the lower stratosphere, NO_x moderates O_3 destruction by combining with hydrogen (HO_x) and halogens (ClO_x, BrO_x) radicals involved in catalytic ozone destruction. It is therefore essential to understand quantitatively the chemistry controlling the levels of stratospheric NO_x and its conversion into NO_y (total nitrogen oxides = NO_x + NO_3 + 2*N_2O_5 + $ClONO_2$ + HNO_3) reservoir species such as N_2O_5 and HNO_3. The partitioning of the NO_y species usually involves gas phase reactions in middle stratosphere and gas phase and heterogeneous reactions in the lower stratosphere. The nitrate radical (NO_3) is an important intermediate in the establishment of the partitioning. Its nighttime chemistry is believed to be relatively simple in the stratosphere with the following three reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R1)}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \quad \text{(R2)}$$

$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M \quad \text{(R3)}$$

[3] NO_3 is produced by reaction of NO_2 with O_3 (reaction 1). This reaction, whose rate constant is strongly temperature dependent, affects the nighttime decay rate of NO_2. The NO_3 sink in the stratosphere is its reaction with NO_2 (reaction 2) which produces N_2O_5. N_2O_5 is a key species in the NO_y partitioning because it is subject to heterogeneous hydrolysis on sulphuric acid particles producing HNO_3, the long-lived NO_y reservoir species. Finally, the other source of NO_3 is the thermal decomposition of N_2O_5 (reaction 3). The NO_3 concentrations are close to zero during the day because it is photolysed extremely quickly in the presence of sunlight.

[4] Although any information on NO_3 levels would be very useful in testing further our knowledge on the NO_y family, NO_3 measurements are scarce. Vertical profiles of NO_3 have been inferred from ground-based measurements [*Smith and Solomon*, 1990; *Aliwell and Jones*, 1996], and from balloon-borne instruments using planets or stars as light sources [*Noxon et al.*, 1978; *Naudet et al.*, 1981, 1989; *Renard et al.*, 1996]. The NO_3 measurement by the "Global Ozone Monitoring by Occultation of Stars" (GOMOS) instrument on board the "Environment Satellite" platform [*Bertaux et al.*, 2000] is the first satellite measurements of this species. The validation of satellite measurements is usually based on direct comparisons against coincident independent measurements (ground-based or even another satellite instrument). This method of validation cannot be applied in the case of GOMOS NO_3 data because, to our best knowledge, there have not yet been independent NO_3 measurements available since GOMOS started operating on March 2002. Nonetheless, the simultaneous measurements of O_3 and NO_2 are strongly coupled to NO_3 chemically. This property of the chemical system NO_3, NO_2 and O_3 allows us to test the self-consistency of the GOMOS measurements of the different species using a numerical photochemical model. This approach is most rigorous in regions where the chemistry of these species is known to be well understood. In order to constrain as well as possible the photochemical model with the GOMOS nighttime measure-

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ments and optimize the choice of initial conditions, the measurements are assimilated in the photochemical model using a variational assimilation scheme. Another important objective of this study is to validate GOMOS NO_3 measurements, albeit in an indirect way, because of the lack of opportunities for a direct validation against independent measurements. The self-consistency test represents also implicitly a test of our quantitative understanding of the chemical couplings between these species. The paper is organized as follows. GOMOS data and the assimilation experiments are described in the section 2 and 3 respectively. The final section is devoted to the presentation of the results and their discussion.

2. GOMOS Data

[5] The GOMOS instrument on board ENVISAT has been launched by the European Space Agency on 1st March 2002. GOMOS is a UV-visible-near IR spectrometer on a sun-synchronous orbit observing stellar occultations [*Bertaux et al.*, 2000]. It provides 400 profiles per day all around the globe of O_3, NO_2, NO_3, H_2O, aerosols and Polar Stratospheric Clouds (PSCs) from 15 to 100 km for O_3 and from 20 to 50–60 km for other constituents. Slant columns of atmospheric constituents are retrieved by the analysis of spectral bands between 250 nm to 675 nm, 756 nm to 773 nm, and 926 nm to 952 nm. Additionally, two photometers operate in two spectral channels, between 470 nm to 520 nm and 650 nm to 700 nm respectively. They are used to correct stellar spectra from scintillations due to small-scale turbulent structures in the atmosphere.

[6] All species are retrieved at the same time by a global minimization of the mean square difference between the measured transmission and the model transmission. Vertical profiles of constituents are obtained from slant columns using an onion peeling inversion technique [*Connor and Rodgers*, 1988] assuming a linear variation of the concentration between 2 layers. The retrieval of NO_2 and NO_3 species is adversely affected by the residual chromatic effect of scintillations on star spectra after the photometer correction [*Dalaudier et al.*, 2001]. This problem is most acute for occultations on stars setting obliquely through the atmosphere. In order to correct for the adverse effect of the scintillation, a new algorithm based on the use of differential absorption spectroscopy (DOAS) [*Platt et al.*, 1979] has recently been developed and implemented in the GOMOS retrieval chain. Two geometries of star setting: a setting more or less vertical (very little influence of scintillation) and an oblique setting (strong influence of scintillation) are selected. We consider the star Beta Carinae (GOMOS star S029, visual magnitude 1.67, temperature 10200 K) and two periods: December 5 to 6, 2002, and January 30 to February 2, 2003. For the first period (December 5 to 6, 2002), the star sets in the latitude band 0–1°N with an angle between 20° and 21° from the vertical. For the second period (January 30 to February 2, 2003), the star sets in the latitude band 16–17°N with an angle between −1° and +1° from the vertical; in this configuration of vertical setting, chromatic effects are strongly reduced because the star light crosses the same turbulent structures at all wavelengths. During both periods, the measurements are made at 22h00 local time and 150° zenith angle, 4 hours after local sunset.

[7] Data are produced using the prototype data chain at ACRI-ST (Sophia-Antipolis, France) that is responsible for providing GOMOS data during the validation phase of the instrument. In the present study we use data obtained with a research retrieval algorithm (version V6.0). In this version, a DOAS spectral inversion is applied for NO_2 and NO_3. A Tikhonov regularization is also performed during the vertical inversion in order to smooth out unphysical oscillations that can appear on the vertical profiles. This reduces the vertical resolution to 3 km for O_3 and 4 km for NO_2 and NO_3. The retrieval algorithm (Version V6.0) will be used operationally at ACRI-ST in the near future to reprocess all the GOMOS data from July 2002 till now. The measurement errors on O_3 are less than 3% typically. The measurement errors on NO_2 and NO_3 are much higher; on average, they are of the order of 35% and 130% respectively. Note that, although the shape of the NO_3 cross sections is well known, uncertainties may exist in their absolute values [*Renard et al.*, 2001]. This is the main source of systematic errors in GOMOS NO_3 measurements. The GOMOS O_3 and NO_2 profiles are then interpolated onto 10 isentropic levels, from 735 K (~28 km) to 1960 K (~48 km). This interpolation uses European Centre for Medium-Range Weather Forecasts (ECMWF) temperature and pressure fields interpolated at the location of GOMOS measurement. The total number of cases considered in this study is 465.

3. Chemical Assimilation

[8] The photochemical box model is described in details by *Khattatov et al.* [1999] and *Marchand et al.* [2003]. The stratospheric photochemical scheme is standard and takes also into account heterogeneous chemistry on sulfuric acid particles assuming a background aerosol loading. Rates constants for the photochemical reactions follow the recommendations of *Sander et al.* [2003]. The photodissociation of HNO_4 in the near infra-red is also included [*Roehl et al.*, 2002].

[9] Initial conditions for the photochemical box model are provided by simulations from the well-established 3-D "REactive Processes Ruling the Ozone BUdget in the Stratosphere" (REPROBUS) CTM [*Lefèvre et al.*, 1994]. The box model is coupled to a variational assimilation scheme in order to constrain it by the GOMOS measurements as well as possible. The variational method assumes that the photochemical model is perfect (no model errors) and hence only the model initial conditions are modified in order for the model simulations to fit the measurements in an optimal way (in a least-square sense) taking into account the measurement errors. The concentrations of all the short lived species are control variables, so, are all adjusted. This chemical assimilation system has been used successfully in the analysis of balloon-borne measurements of polar O_3 and NO_2 [*Marchand et al.*, 2003]. A somewhat similar approach is adopted here. Only the simultaneous measurements of O_3 and NO_2 are assimilated. These species determine to a large extent NO_3 levels. The other parameters are temperature and air density which are taken from ECMWF analysis. The methodology is the following. First, each pair of NO_2 and O_3 GOMOS measurements are assimilated simultaneously in the photochemical model integrated during 1 day at the location of the GOMOS measurements (air motion is

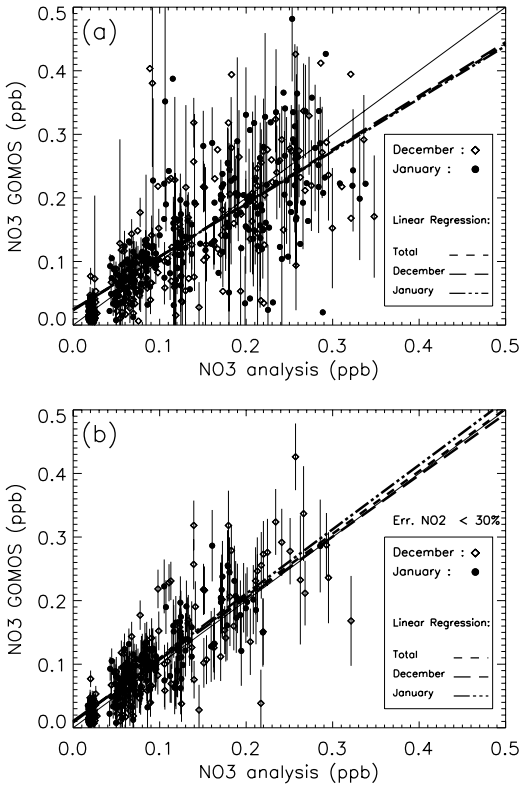

Figure 1. GOMOS NO_3 measurement as a function of analyzed NO_3 for (a) all the cases and (b) for cases when NO_2 error measurements is less than 30%. NO_3 error measurements are indicated with vertical lines. The linear regressions for the different periods are represented with dashed lines. The 1-to-1 line is represented with a thin black line.

neglected). The chemistry of NO_3 is sufficiently rapid in most of the considered altitude interval that neglecting the effect of transport should result in relatively small errors in the analysis. The photochemical model is forced by the ECMWF temperature and pressure. Then, the analyzed NO_3 (i.e., NO_3 calculated by the model after assimilation of GOMOS NO_2 and O_3 data) is then compared to the corresponding GOMOS NO_3 measurement. It is worth pointing out that there are several potential sources of biases in analyzed NO_3. As the photochemical model is forced by GOMOS O_3 and NO_2 measurements, systematic errors on these quantities could translate into biases in analyzed NO_3. However, preliminary tests show that, varying the values of GOMOS O_3 and NO_2 within measurement errors before their assimilation has little impact on the overall results. Errors in analyzed NO_3 could also originate from biases in the kinetic data used by the model. For example, the uncertainties in the rate constants of reactions 1 and 2 at 298 K have been estimated to be about 15% and 20% respectively [*Sander et al.*, 2003].

4. Results and Discussion

[10] The analysis (analyzed O_3, NO_2 and NO_3 calculated after assimilation of GOMOS O_3 and NO_2 data) is performed on the 465 GOMOS measurements. In all the cases, the analyzed O_3 and NO_2 match the corresponding O_3 and NO_2 measurements within 8.4 e-5% et 9.3 e-3% respectively, which is a sign of a successful model constraint. The NO_3 measurements are plotted as a function of the corresponding analyzed NO_3 in Figure 1a. The early December (oblique star setting) and the late January (vertical star setting) data points are represented with different symbols. Measurement errors for GOMOS NO_3 are indicated with vertical lines. The slope of the linear regression on all the data points is 0.834 (0.843 for the oblique star setting occultations and 0.828 for the vertical star setting occultations). The linear regression slopes are close to each other. They all deviate significantly from the 1-1 line. A sensitivity test has been performed using the changes to the rate constants of reaction 1 and 3 suggested by *Aliwell and Jones* [1996]. The results show that the suggested changes to the N_2O_5 equilibrium rate constant rate tend to worsen the agreement with GOMOS NO_3 in the upper stratosphere. The slope of the linear regression (GOMOS NO_3 versus analyzed NO_3) becomes 0.61 (see the auxiliary material[1] for details).

[11] There are some points in Figure 1a which deviate very strongly from the 1-1 line. These outliners often correspond to higher altitude levels and are characterized by unusually large errors in GOMOS NO_2 and NO_3. In order to remove these cases from the analysis and focus on the most reliable data, only cases corresponding to GOMOS NO_2 data with errors of less than 30% are considered in Figure 1b. The total number of cases left after this filtering is 296. The linear regression slope is 0.98 ± 0.04 (0.97 ± 0.072 for the oblique star setting occultations and 1.01 ± 0.043 for the vertical star setting occultations). One can notice that, as in Figure 1a, there is no statistically significant difference between the linear regression slopes on the two types of star occultations. This confirms the ability of the DOAS retrieval algorithm to remove the strong adverse effect of scintillation in case of oblique star setting occultations. If cases corresponding to GOMOS NO_2 data with errors of less than 50% are considered (not shown), the linear regression slope deviates a bit from unity. In general, the more stringent the selection criteria on GOMOS measurement errors, the closer the linear regression is to the 1-1 line.

[12] There seems to be a substantial amount of scatter in the plots 1-a and 1-b. Nonetheless, one has to keep in mind that the number of data points is very high with many points covering each other in the vicinity of the 1-to-1 slope. In order to have a better idea of the variability as a function of altitude, analyzed NO_3 and GOMOS NO_3 are averaged over each isentropic level and plotted against each other in Figures 2a and 2b. The standard deviation on the isentropic means of GOMOS NO_3 and of analyzed NO_3 are also indicated with vertical and horizontal lines respectively. Most of the data points are found very close to the 1-1 line. The slopes of the linear regressions (0.88 ± 0.05 for Figure 2a and 0.94 ± 0.05 for Figure 2b) do not change very significantly compared to Figures 1a and 1b.

[13] In order to save computing time, some global Chemistry Transport Models (CTMs) use a steady-state approximation instead of calculating explicitly NO_3 at night [*Lefèvre et al.*, 1994]. They assume that the thermal decomposition of N_2O_5 is negligible. Therefore, when NO_3 is in

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL019631.

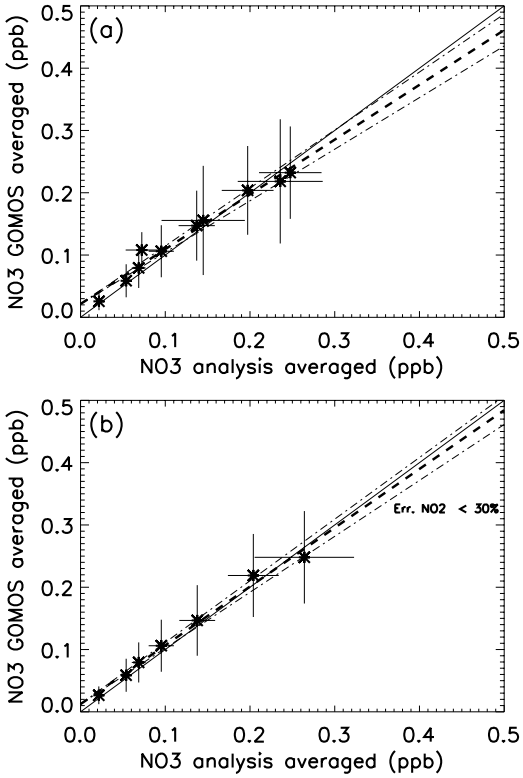

Figure 2. Same as Figure 1 but GOMOS NO_3 measurement and analyzed NO_3 are averaged over isentropic levels. The isentropic levels are 735, 900, 990, 1100, 1210, 1350, and 1510 K. Note that, due to the lack of NO_2 data with errors of less than 30% at 1670, 1830 and 1960 K, no datapoints are represented for these levels. The standard deviations of the isentropic means of GOMOS NO_3 and of mean analyzed NO_3 are indicated with vertical and horizontal lines respectively.

steady-state, the nighttime NO_3 concentration becomes simply proportional to O_3 and independent of NO_2 [*Sanders et al.*, 1987],

$$[NO_3]_{eq} = \frac{k_1}{k_2}\frac{[O_3]}{[M]} \quad (1)$$

where $[NO_3]_{eq}$ is the steady-state concentration, k_x the rate constant of reaction R_x (R_1, R_2 or R_3), $[O_3]$ the concentration of O_3 and [M] the concentration of the air density.

[14] Steady-state NO_3 are found to match well analyzed NO_3 below 40 km (not shown). It shows that chemical data assimilation was not needed below 40 km for analyzing the considered GOMOS data. Expression (1) was sufficient. Therefore the comparison between analyzed NO_3 and GOMOS NO_3 below 40 km is simply a consistency test of GOMOS NO_3 and O_3, ECMWF density and the ratio of the two rate constants (k_1 and k_2). Above 40 km, expression (1) cannot be applied because the thermal decomposition of N_2O_5 cannot be neglected. It is worth pointing out that a good match between steady-state NO_3 and analyzed NO_3 in our cases does not necessarily mean that NO_3 is strictly in steady-state. Indeed, it can take NO_3 several hours to reach its equilibrium value after sunset. Expression (1) is strictly applicable below 35 km where the NO_3 diurnal variation looks like a step function.

[15] The analyzed NO_3 is more or less independent of the value of GOMOS NO_2 measurement below 40 km in our cases. The only source of random errors in analyzed NO_3 is the random errors of GOMOS O_3 which are very small. This partly explains why the agreement between analyzed NO_3 and GOMOS NO_3 is better when the upper stratospheric cases are removed from the analysis. Overall, the fact that linear regression slopes are so close to unity, especially when the most reliable GOMOS data are considered (see Figure 1b), indicate that there is no substantial bias in GOMOS NO_3 data. It also suggests that O_3, NO_2 and NO_3 GOMOS measurements are self consistent chemically and that the nighttime NO_3 chemistry is well understood.

[16] **Acknowledgment.** The superb work of the GOMOS team is gratefully acknowledged.

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