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Test of the night-time polar stratospheric NO₂ decay using wintertime SAOZ measurements and chemical data assimilation

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[1] Chemistry Transport Models (CTMs) tend to underestimate very severely NO₂ concentrations in the polar lower stratosphere during the winter suggesting that either the NO_x sink is overestimated or a source of NO_x is missing in models. We study the night-time decay of polar NO₂ because it is controlled by the reaction between NO₂ and O₃ which is thought to be the main NO_x sink at high latitudes winter. The model-calculated night-time decay of polar NO₂ is tested using solar occultation measurement of NO₂ and O₃ taken within the Northern polar vortex by the "Système d'Analyse par Observation Zénithal" (SAOZ) instrument on board of a long duration balloon in February 2000. A trajectory analysis is performed in order to find air parcels which have been sampled at sunset and at sunrise by the SAOZ instrument and have stayed in the dark between the measurements. Sunset (or sunrise) SAOZ measurements are then assimilated in a trajectory photochemical model in a variational mode and compared to the corresponding sunrise (or sunset) SAOZ measurements which are called validation measurements. The results are used to assess the ability of the model to reproduce the observed night-time evolution of NO₂. Overall, there is a good agreement between analyzed NO₂ and validation measurements indicating that the night-time chemistry of NO₂ appears to be properly described by the model. The results do not hint at all at the existence of a NO_x source, and certainly not a source strong enough to counteract the NO₂ sink (NO₂ + O₃ reaction).

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.
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1. Introduction

[2] It is now well established that stratospheric ozone has been declining, particularly at high latitudes, during the past 2 decades mainly as a result of the build up of chlorine and bromine containing species. Though NO_x (NO + NO₂) species are not directly destroying ozone in the polar stratosphere during the winter, their removal from the gas-

phase is essential to polar ozone depletion. However, there are still deficiencies in our understanding of the photochemistry of NO_x species in the lower stratosphere. Chemical transport models seem to underestimate NO₂ concentration and the NO_x/NO_y ratio in the lower stratosphere. For example, midlatitudes measurements under different aerosol loading conditions [Sen *et al.*, 1998] have indicated that, in some cases, models may underestimate NO₂ by up to 30% between 15 and 21 km.

[3] The discrepancy is much more pronounced at high latitudes during the winter. Three-dimensional (3-D) chemistry transport model simulations predict extremely low NO₂ levels, of the order of few tens of pptv or even less, in the polar vortex below 22 km, whereas NO₂ measurements inside the Arctic polar vortex range from 80 to 300 pptv [Lary *et al.*, 1997; Payan *et al.*, 1999]. The recent reevaluation of rate constants of the O + NO₂ [Gierczak *et al.*, 1999], OH + HNO₃ [Brown *et al.*, 1999a] and OH + NO₂ [Brown *et al.*, 1999b] tend to increase model calculated NO₂ and the NO_x/NO_y ratios. However, the changes are not sufficient to account for all the differences between models and measurements, especially at high latitudes [Gao *et al.*, 1999; Kondo *et al.*, 2000]. The extremely low NO_x levels predicted by models at high latitudes during the winter are due to the lack of sunlight which is expected to favor the conversion of NO_x into reservoir species, such as N₂O₅ and HNO₃. The disagreement between models and measurements suggest that a source of NO_x might not be accounted for in models, and that this source is able to counter the effect of the NO_x sink which operates on a time scale of days typically. Since the discrepancy is also found at high latitudes during the summer (on air parcels with continuous solar exposure), the parameterization of the N₂O₅ hydrolysis reaction is unlikely to be the cause [Gao *et al.*, 1999]. One of the favored hypothesis is the occurrence of heterogeneous reactions, for example on carbaceous aerosols which would convert back HNO₃ into NO_x [Lary *et al.*, 1997].

[4] The night-time NO₂ chemistry is thought to be very simple, with its concentration decaying steadily during the night due to the reaction with O₃. If there was a substantial source of NO_x competing with the night-time NO₂ sink (NO₂ + O₃ reaction), the night-time NO₂ evolution should not follow the exponential decay. This should be most noticeable in night-time NO₂ data. The objective of this study is to test whether wintertime balloon observations of night-time NO₂ hint at a significant NO_x source at high latitudes in the polar vortex, where the discrepancy between

models and measurements is well established. For this purpose, we analyze solar occultation measurements of NO₂ and O₃ taken within the Northern polar vortex by the “Système d’Analyse par Observation Zénithal” (SAOZ) instrument performed on board of a Infra-Red Montgolfier (MIR) long duration balloon in February 2000 during the THird European Stratospheric Experiment on Ozone (THESEO) campaign. Although the MIR balloons tend to move up during the day and down during the night by several kilometers, some successive measurements are found to be quasi-Lagrangian (measurements in the same flow) [Pommereau *et al.*, 2002]. This offers the opportunity to probe from time to time the same air masses at sunset and at sunrise. In order to exploit the full potential of these data and optimize the data analysis, the SAOZ measurements are assimilated in a trajectory photochemical model run in variational mode. The variational assimilation allows the photochemical model to be constrained by the measurements in an optimal way. The results of the assimilation are used to test the ability of the model to reproduce the observed night-time evolution of NO₂, and hence investigate the possibility of a missing NO₂ source. The paper is organized as follows. The balloon measurements as well as the assimilation experiments are described in the next section. The final section is devoted to the presentation of the results and their discussion.

2. Methodology

2.1. Data

[5] The wintertime O₃ and NO₂ data have been obtained by solar occultation in the visible range using a SAOZ spectrometer flown in the polar vortex onboard a long duration Infra-Red Montgolfier balloon during the THESEO-SOLVE campaign [Pommereau *et al.*, 2002]. A total of 8 simultaneous O₃ and NO₂ profiles (4 sunsets, 4 sunrises) have been recorded during the February 20th–23th period between about 350 K and 650 K with a vertical resolution of about 1.2 km. The precision of the O₃ measurements in the lower stratosphere is 2% (one standard deviation) with a total accuracy of 4%. The precision of the NO₂ measurements varies from 5% at 550 K (10% accuracy) to 20% (30% accuracy) at 350 K typically. The relative error increases sharply in regions denoxified by PSCs activity because of the extremely small concentrations of NO₂. Only NO₂ measurements with an error of less than 50% are considered to be reliable enough for our purposes. Indeed, NO₂ variations at night are of the order of 20 to 60% in our conditions.

2.2. Chemical Assimilation

[6] The night-time decay of NO₂ is thought to be simply determined by its reaction with O₃ whose rate constant is strongly temperature dependent. In principle, if the O₃ mixing ratio, pressure and temperature are known, the entire NO₂ evolution can be inferred from a single night-time measurement of NO₂ [Toumi *et al.*, 1991]. Therefore, the SAOZ O₃ and NO₂ data should provide sufficient constraints for testing the night-time NO₂ decay. However, the SAOZ measurements are not exactly night-time measurements. They are sunset and sunrise measurements (zenith angle of 90°). At sunset, NO is completely converted into NO₂ via its reaction with O₃ and at sunrise, part of the NO₂

is converted back into NO via the NO₂ photolysis. Therefore, the SAOZ measurements cannot be used on their own to derive nighttime NO₂. It is necessary to use a photochemical model for linking the sunset/sunrise NO₂ measurements to night-time NO₂. In addition, the SAOZ measurements cannot be used to initialize directly the photochemical model because of the strong NO₂ variations at twilight. It is necessary to couple the photochemical model to a variational assimilation scheme in order to find the model initial conditions giving an optimal match between model calculations and the SAOZ measurements. The photochemical box model is described in Khattatov *et al.* [1999]. The model automatically generates photochemical kinetic equations from a list of reactions and a list of species. The stratospheric photochemical scheme includes 58 chemical reactions, 16 photodissociation reactions representing the O_x, HO_x, NO_y and Cl_y chemistry. Rates constants for the photochemical reactions follow the recommendations of DeMore *et al.* [2003]. The photodissociation of HNO₄ in the near Infra-Red is also taken into account [Coleen *et al.*, 2002]. Mixing ratios of long-lived species and of sulfate aerosols are held constant. Heterogeneous reactions on sulfuric acid particles are taken into account assuming a background aerosol loading. The model does not describe Polar Stratospheric Cloud (PSC) chemistry. Nonetheless, the European Centre for Medium-Range (ECMWF) indicated that the temperature did not drop below the threshold for PSC formation for all the measurements analyzed here. Initial conditions for the photochemical model are provided by 3D simulations from the “REactive Processes Ruling the Ozone BUDget in the Stratosphere” (REPROBUS) Chemistry Transport Model performed for the 1999–2000 winter [Hoppel *et al.*, 2002]. The photochemical box model is run in a trajectory mode for realism and is coupled to a variational assimilation scheme in order to constrain it by the SAOZ measurements as well as possible. In the variational approach, the photochemical model is assumed to be perfect (no model errors) and the model initial conditions are adjusted in order for the model predictions to fit the simultaneous measurements of O₃ and NO₂ in an optimal way (in a least-square sense).

2.3. Selection of the Coincidence Cases

[7] The procedure includes 3 steps. First, 5 days backward and forward trajectories starting from the position of each SAOZ measurement are calculated using T42 ECMWF analyses (8 profiles × 21 isentropic levels ranging from 300 to 650 K = 168 forward/backward trajectories). Second, each pair of NO₂ and O₃ SAOZ measurement are assimilated simultaneously in the photochemical model running along the corresponding trajectory. Note that, when discussing a particular trajectory and the associated analysis, the measurements which are assimilated will be referred to as assimilation measurements in the text.

[8] Finally, the forward/backward trajectories are also used to identify the air parcels which have or will be sampled again by the SAOZ instrument. We consider that an air parcel moving along a trajectory is sampled again if the new SAOZ measurement is made within 15 minutes and within 1000 km of the air parcel. The selected measurement is then compared to the analysis (assimilated measurement). Note that, the selected measurement will be referred to as

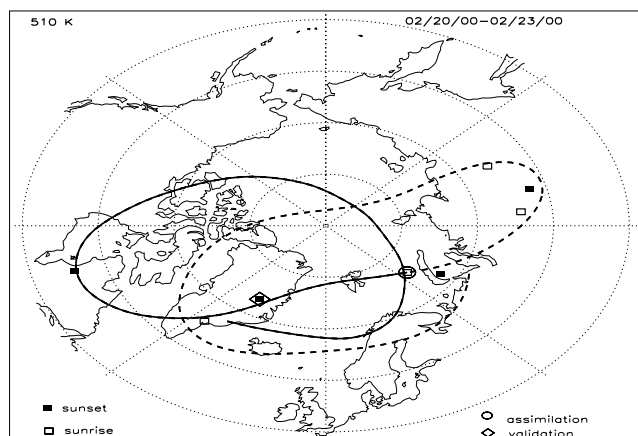


Figure 1. 5 days backward/forward trajectory (solid/dashed line) corresponding the 22/2/2000 sunrise SAOZ measurement at 510K. Positions of the sunset (solid square) and sunrise (empty square) SAOZ measurements between 20/2/2000 and 23/2/2000 are also shown. The assimilation (22/2/2000, at sunrise) (circle) and the validation (21/2/2000, at sunset) (diamond) measurements are also indicated.

validation measurement in the text. In order to study the night-time chemistry only, we look for a validation measurement at the next sunrise if the assimilation measurement is very small, about 1%. The analyzed NO₂ follows the expected pattern at night with an exponential decay. The

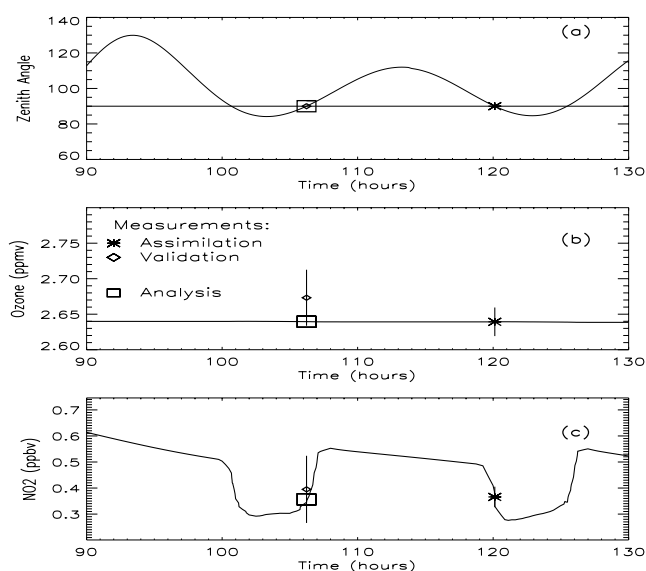


Figure 2. Time evolution of the zenith angle (a), analyzed O₃ (b) and analyzed NO₂ (c), along the trajectory shown in Figure 1. Assimilation (star), validation (diamond) measurements, and analyses (square) are also indicated.

in Danilin *et al.* [2002]. In total, 21 cases of coincidence are found.

3. Results and Discussion

[9] An example of case study is described below. The trajectory corresponding to the 22/2/2000 SAOZ measurement (4th profile, at sunrise) at 510K is shown in Figure 1. The positions of the other measurements are also indicated. The 21/2/2000 measurement (3th profile, at sunset) fulfills the coincidence criteria described in section 2.3. This measurement is made within 15 minutes and at about 600 km of the moving air parcel which, according to the trajectory, will be perfectly sampled by the SAOZ instrument 12 hours later on the 22/2/2000 (4th profile at sunrise). In this case, the 21/2/2000 sunset measurement is the validation measurement and the 22/2/2000 sunrise measurement is the assimilation measurement. The analysis (i.e. model simulation after adjustment to the assimilation measurements along the corresponding trajectory) is presented in Figure 2. The analyzed O₃ and NO₂ and the zenith angle are plotted as a function of time. The O₃ and NO₂ mixing ratios of the assimilation and validation measurements which bracket the NO₂ night-time decay are also indicated. The analyses appear to match the assimilation O₃ and NO₂ measurements perfectly. O₃ has such a long photochemical lifetime in the polar lower stratosphere that the mixing ratio of the analyzed O₃ is almost constant. The difference between the analyzed O₃ and the validation measurement is very small, about 1%. The analyzed NO₂ follows the expected pattern at night with an exponential decay. The

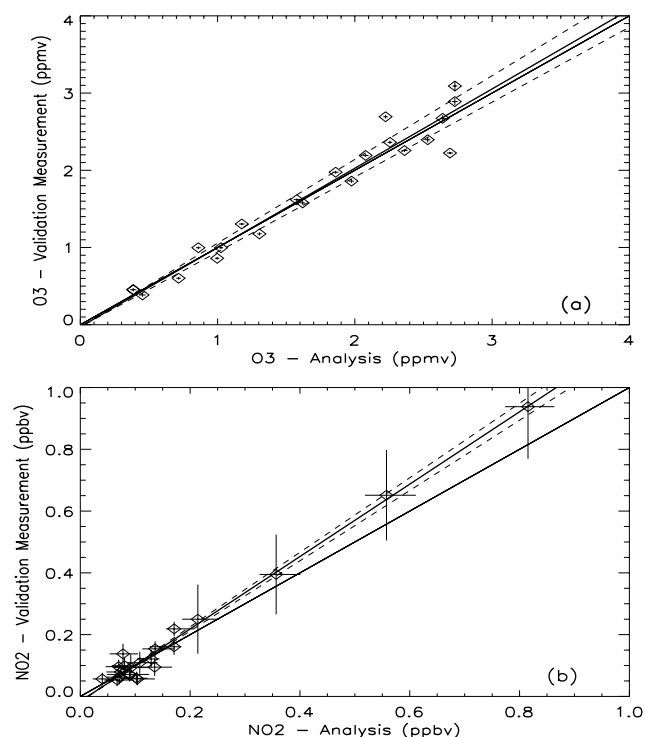


Figure 3. Validation measurements as a function of the analysis for O₃ (a) and NO₂ (b). The linear regression are represented with the black thick line along with the 1 σ error on the fit (dashed line).

difference between the analyzed NO₂ and the validation measurement is relatively small (8%) and well within the measurement errors. This result does not indicate the existence of a bias in the photochemical model.

[10] The same analysis has been performed on the 20 other coincidences. The results are summarized in Figure 3. In all the cases, the analyzed O₃ and NO₂ are within 0.03% and 4% of the assimilation measurements respectively, confirming the quality of the assimilation. The corresponding validation measurements of O₃ and NO₂ are plotted as a function of the analyzed O₃ and NO₂ in Figures 3a and 3b respectively. The errors of the validation measurements are represented with vertical lines. The horizontal lines represent analysis errors which are estimated by adding or subtracting the measurement errors to the values of the assimilation measurements before performing two additional assimilation runs. The differences between the validation measurements and the corresponding analyzed O₃ are small. The slope of the linear regression of the O₃ correlation plot (see Figure 3a) is 1.03 (±0.06), with a linear correlation coefficient of 0.97. As O₃ can be considered as a dynamical tracer in the polar lower stratosphere, this result gives some confidence in the quality of the trajectories. There is more scatter in the correlation plot between the analyzed NO₂ and the corresponding validation measurements. The slope of the linear regression is 1.17 (±0.034), with a linear correlation coefficient of 0.992. Overall, the agreement is reasonably good, suggesting that the night-time evolution of NO₂ is properly described by the model. Our results clearly do not show any evidence for a significant NO_x source at night, and certainly not a source able to compete with the NO₂ sink. Therefore, the glaring NO₂ discrepancy between models and measurements at high latitudes in winter does not appear to originate from a misunderstanding in the nighttime chemistry. Assimilating only one pair of simultaneous O₃ and NO₂ measurements and comparing the resulting analysis to another pair of measurements allow us to look for a model bias in analysis-validation correlation plots, and test the sensitivity of the results to the coincidence criteria without having to perform additional assimilation runs. Assimilating both pairs of measurements would lead to similar conclusions, but would require more assimilation runs when varying the coincidence criteria and the assimilation diagnostics which are not readily defined.

[11] A number of sensitivity tests have been performed. Reasonable changes in the coincidence criteria do not alter the results very significantly, leaving the conclusions unaffected. In order to test the sensitivity of the results to the meteorological analysis, the same assimilation experiment is carried out, but with trajectories calculated using U.K. Meteorological Office (UKMO) analysis. A more pronounced scatter is found in the analyses-validation measurement correlation plots (not shown). It was expected because the UKMO analyses are usually found to be less reliable than the ECMWF analyses for trajectory calculations [Knudsen et al., 2001]. The slope of the linear regression for the NO₂ correlation plot is 0.71 which is still too close to unity for inferring the existence of a strong night-time NO_x source.

[12] The number of cases considered (21 cases) is probably too small to prove beyond doubt that the observed NO₂ night-time decay is exactly reproduced by the model.

Nonetheless, the results do not hint at the existence of a night-time source of NO_x in the polar lower stratosphere during the winter. This implies that renoxification processes such as the heterogeneous conversion of HNO₃ into NO_x on carbonaceous aerosols [Lary et al., 1997] does not operate under the conditions considered here and are certainly not able to counterbalance the NO₂ sink. The very large underestimation of NO₂ in CTMs at high latitudes in winter is still an unresolved issue. As the NO₂ nighttime chemistry appears to be well understood, it might be worth looking for the origins of the NO₂ problem in the daytime chemistry at high zenith angles.

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