

INTERACTION OF PHOTOCHEMICAL AND RADIATIVE PROCESSES IN THE STRATOSPHERE: AN APPLICATION ON THE RETRIEVAL OF CONCENTRATION PROFILES FROM SATELLITE MEASUREMENTS

CONSTANTINOS I. CARTALIS*

Department of Atmospheric, Oceanic and Space Sciences, Space Physics Research Laboratory, The University of Michigan, Ann Arbor, Michigan, U.S.A.

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Abstract. A new method is developed to determine the concentration profiles of chemical species from satellite measurements. The method takes into account the interaction of photochemical and radiative processes in the stratosphere and is applied for chemical species (nitric oxide and nitrogen dioxide) experiencing large diurnal changes. It is found that if the interaction of the photochemical and radiative processes is neglected, that is if the temporal and spatial variations of NO and NO₂ are not considered in the radiative transfer calculations, the resulting errors for the concentration profiles for altitudes less than 20 km reach 100 and 5% respectively, for both sunset and sunrise. A photochemical scheme is developed capable of providing the mixing ratio profiles of NO and NO₂ for different latitudes, altitudes and seasons and a retrieval code combining an iterative inversion algorithm, working from top of the atmosphere downwards, and a parameterization of the variability of NO and NO₂ is also constructed. The method is used to examine the accuracy of the retrieval of the vertical concentration profiles and the new results show that the recovered profiles are in good agreement (error 5–15%) with measured profiles (WMO, 1985) and reflect the trends of NO and NO₂ at sunset and sunrise.

1. Description of the Problem

In most retrieval algorithms, the chemical composition of the species under investigation is assumed to remain constant with time during the measurements. Such an approach is justified for ozone and water vapor but fails for the case of NO and NO₂. The large spatial and temporal variations of NO and NO₂ around sunrise and sunset, need to be taken into account in any attempt to invert their measured transmittances to obtain the concentration profiles.

Consider Figure 1, which describes the way the atmosphere is modeled for the treatment of the problem. If the spatial and temporal variations of NO and NO₂ are neglected, i.e., if the NO and NO₂ concentrations are assumed to remain constant at locations 1, 2, 3, there will be an underestimation (overestimation) of NO (NO₂) at sunset and sunrise. Depending on the altitude, the errors for NO range from about 5% for altitudes between 42 and 30 km to 100% for altitudes

* Present affiliation: Laboratory of Meteorology, Department of Applied Physics, University of Athens, Greece.

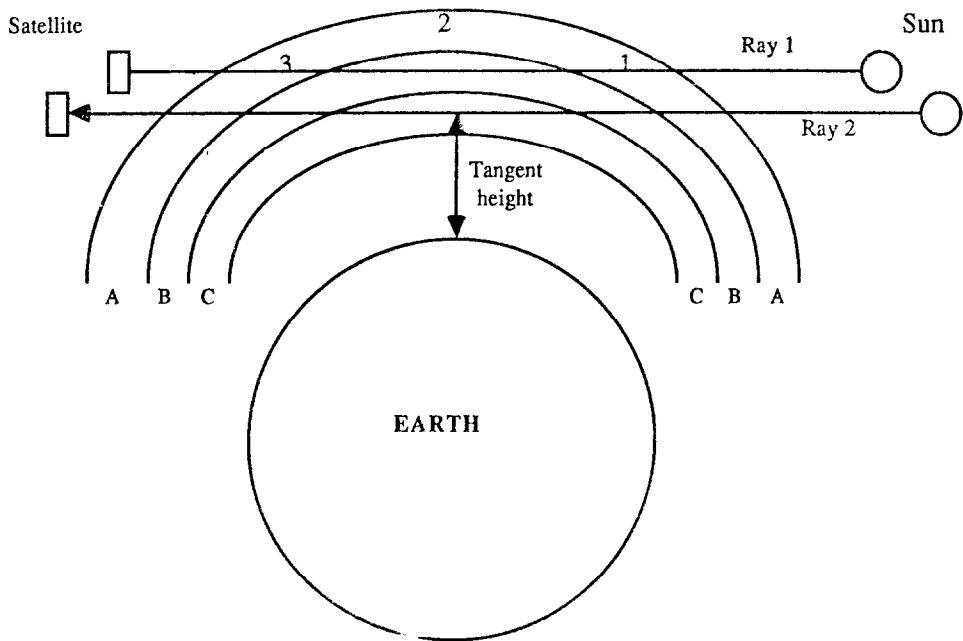


Fig. 1. Geometry illustrating the model of the atmosphere.

less than 18 km. For NO_2 the errors are significantly lower, reaching a maximum of 4 to 5% at the lower altitudes (Cartalis and Drayson, 1988).

2. The Photochemistry of Sunset and Sunrise

Nitric oxide and nitrogen dioxide experience rapid, large concentration changes at sunrise and sunset. Their rapid interconversion depends mostly on sunlight and ozone. Since the lifetimes of NO and NO_2 are of the order of few minutes at sunrise and sunset, the interpretation of solar occultation measurements needs to incorporate the temporal and spatial variations of NO and NO_2 .

The oxides of nitrogen included in this study are NO , NO_2 , HNO_3 , N_2O_5 and NO_3 , but the major concern is focused on NO and NO_2 . The NO_x , HO_x and ClO_x families will play important roles in a complete photochemical scheme. Difficulties arise due to the strong coupling between various reactive species because coupling will result in the inability to separate the roles of individual species. Family analysis allows us to gain insight into the important processes and interactions that affect stratospheric photochemistry. In addition families may overlap, allowing a number of chemical species to participate in two families.

A photochemical model is developed capable of simulating the concentration variations of NO and NO_2 at sunset and sunrise. A more fully detailed description of the photochemical model can be found in Cartalis (1989).

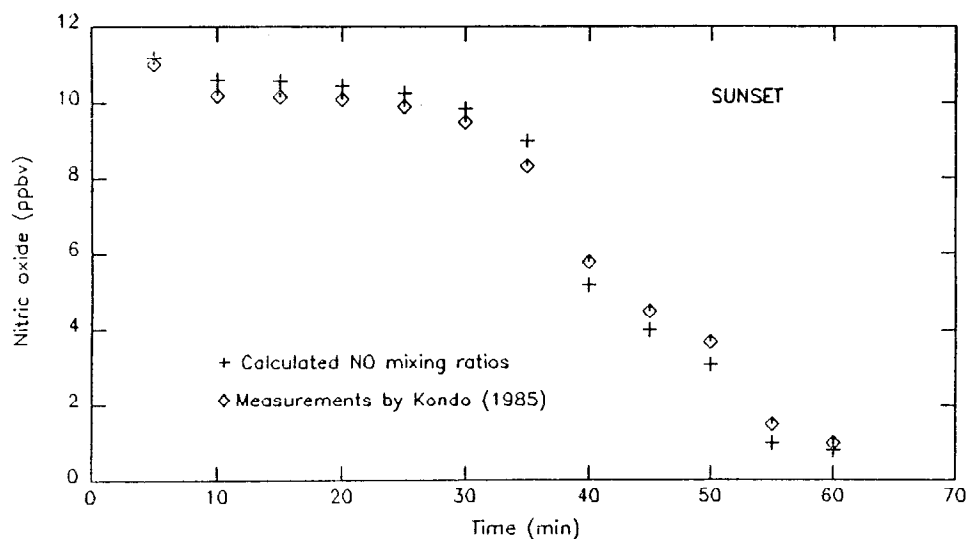


Fig. 2. Results of the photochemical scheme and observations by Kondo *et al.* for NO ($\varphi = 45^\circ$ N, $z = 32$ km, Fall).

3. Results of the Photochemical Scheme

The computer code for solving coupled differential equations (Whitten and Hogo, 1979) is used to solve the large set of nonlinear differential equations derived from the developed photochemical scheme. The code uses a divided-difference formulation of Gear's method with time steps of 5 min. The set of equations is difficult to solve because of its mathematical stiffness (a mathematical system is stiff if it contains eigenstates with greatly different time constants), especially at times close to sunset and sunrise where the photodissociation rates change rapidly.

The recent temperature and temperature and pressure dependent rate constants are used for the second order and third body reactions respectively (DeMore *et al.*, 1987). The solution of the set of non-linear differential equations will depend on the temperature and pressure profiles of the atmosphere, the rate constants of the non-photochemical reactions, the photodissociation rates and the initial values of the chemical species which take part in the photochemical scheme.

The photochemical scheme was tested for different atmospheric conditions and various geographic locations. To test its validity the NO results obtained for latitude of 45° N, altitude of 32 km and atmospheric conditions (temperature and pressure) for the month of September are compared to the observations by Kondo *et al.*, (1988). Figure 2 shows the results of the photochemical scheme used in this study and the measurements by Kondo. The time scale of the abscissas is referred to the time - in minutes - during the last hour before sunset. If we take into account the number of assumptions employed for the calculation of photodissociation rates, and the uncertainty of the albedo value of Kondo's measurements, the 10-15% discrepancies in the NO mixing ratios are satisfactory.

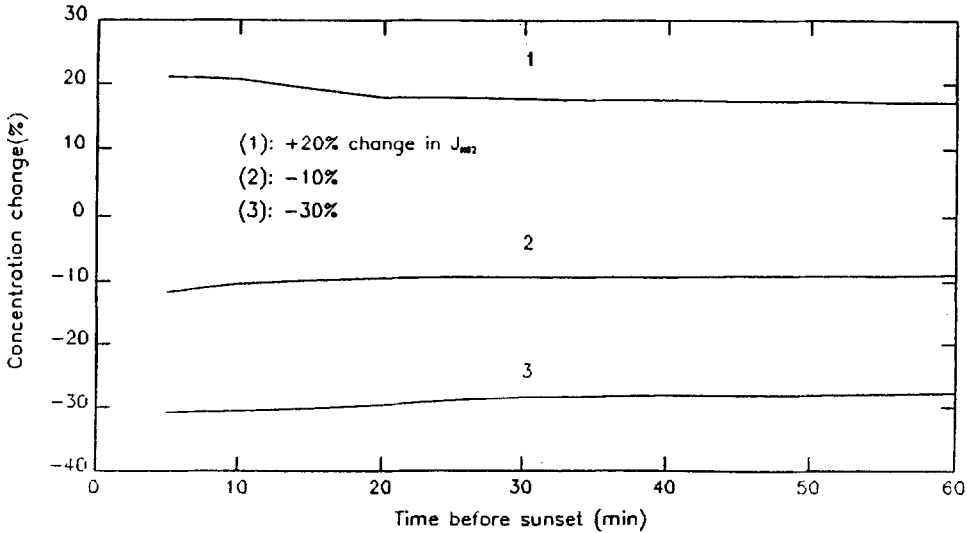


Fig. 3. Percentage changes of the NO mixing ratio if the photodissociation rates of NO_2 are changed by -10%, -30% and +20%.

4. The Parameterization of the Photochemistry of NO and NO_2

The fundamental reaction which controls the photochemical cycles of NO and NO_2 at sunset and sunrise, is the photodissociation of NO_2 due to sunlight.

Figure 3 shows the percentage changes of the NO mixing ratio if the photodissociation rates of NO_2 are changed by -10%, -30% and +20%. In other words the photochemical scheme is run for the correct set of photodissociation rates of NO_2 corresponding to a particular location, altitude and season and the resulting NO mixing ratios are compared to those resulting from the same photochemical scheme and for the same state of the atmosphere but for perturbed photodissociation rates of NO_2 . It is seen from Figure 3 that changes of -10, -30 and 20% in the photodissociation rates of NO_2 result in percentage changes in the mixing ratio of nitric oxide of about the same order. This correlation is expressed mathematically as a function of latitude, season, altitude, temperature and pressure profile and time of the day (sunset or sunrise).

Figure 4 shows the results of the photochemical scheme for sunset, for the month of January, for latitude of $15^\circ N$ and for altitude of 32 km. The results correspond to the time interval starting one hour before sunset and it is seen that at the beginning of the hour (larger photodissociation rates correspond to the beginning of the hour), the NO changes are very small but start increasing later. The data points are fitted with a second order polynomial

$$Y = 0.3043 + 17.98 * X - 11.985 * X^2$$

where Y is the NO mixing ratio and X is the photodissociation rate of NO_2 . This calculation approach is followed for both sunrise and sunset and resulted in four

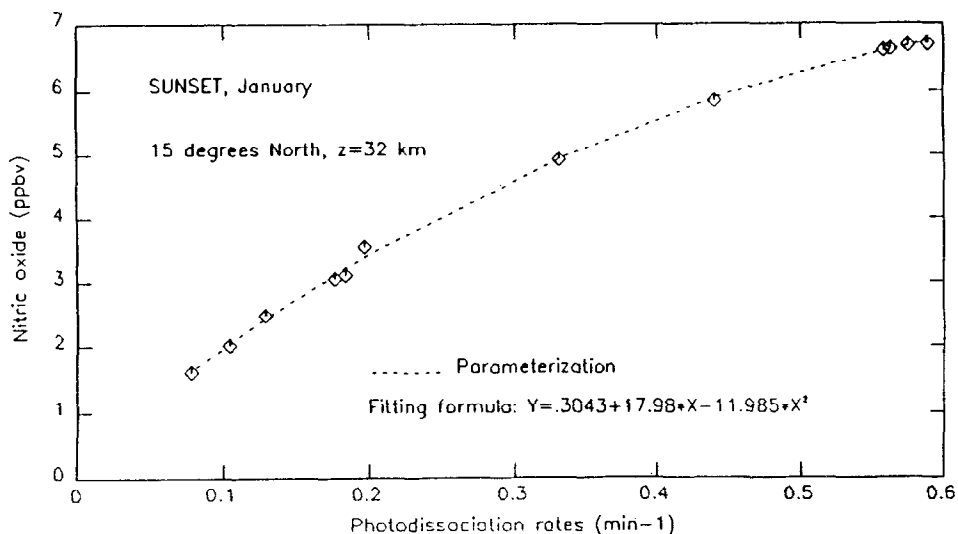


Fig. 4. Curve-fitting for selected case and for the hour of sunset (larger photodissociation rates correspond to the beginning of the hour before sunset). In the fitting formula Y is the NO mixing ratio and X is the NO_2 photodissociation rate.

sets of formulas (NO sunset, NO sunrise, NO_2 sunset, NO_2 sunrise). The sets of formulas simulate the mixing ratio profiles of NO and NO_2 using as input such parameters as the tangent altitude, the latitude, the period of the day (sunset and sunrise) and the value of the photodissociation rate. The seasonal variability of NO and NO_2 is taken into account through the seasonal dependence of the photodissociation rates of NO_2 on season and the variability of the initial values used to initiate the photochemical scheme.

For NO and NO_2 the general formulas for sunset and sunrise are:

For NO:

$$N = A + B * PH + C * PH^2 \quad 42 < z \leq 28 \text{ km}$$

$$N = A * PH \quad 28 < z \leq 14 \text{ km}$$

For NO_2 :

$$N = A + B * PH + C * PH^2 \quad 42 \leq z \leq 24 \text{ km}$$

$$N = A + 10 \quad 24 < z \leq 10 \text{ km}$$

where N is the mixing ratio of NO or NO_2 in ppbv, PH the photodissociation rates of NO_2 in min^{-1} , and A, B, C coefficients which vary with tangent altitude, latitude and period of day (sunset or sunrise).

Due to the extremely low mixing ratios of NO at altitudes of 12 and 10 km, the

parameterization scheme does not reproduce the mixing ratios of NO at these altitudes.

The formulas and coefficients are based in part on scattering computations for specified model cloudless atmospheres. Therefore they are also functions of water droplets, zenith angle, surface albedo, dust particles and the ozone distribution. These parameterization formulas allow the concentration of NO and NO₂ to be treated as variables, permitting the retrieval model to incorporate changes in the NO and NO₂ stratospheric composition at sunset and sunrise.

5. The Inversion Algorithm

The main objective of the inverse algorithms of this research work is to retrieve the vertical composition structure of nitric oxide and nitrogen dioxide in the stratosphere.

It is useful to separate the retrieval model conceptually into two parts:

- the treatment of the photochemistry of NO and NO₂ at sunset and sunrise by updating their concentration profiles;
- the iterative inversion algorithm.

The first part of the model is treated via the parameterization formulas which are described in the previous section. The second part of the model consists of the calculation of the transmission functions and the iterative process. Although line-by-line calculations provide the most accurate transmittance values, we chose to use the New Random model (or Malkmus model) for the following reasons:

- the main purpose of this study is to devise and demonstrate a scheme for incorporating the photochemistry of NO and NO₂ at sunset and sunrise into an inversion algorithm, rather than the optimization of the inversion itself;
- the absolute accuracy of the transmittance values of NO and NO₂ and the modulation function of NO is not important in this study. The model can be modified to calculate the transmittances and the NO modulation using methods based on line-by-line calculations for the inversion of the satellite data when it becomes available;
- if relatively wide spectral channels are used for the investigation of NO and NO₂, line-by-line calculations require large amounts of computational time;
- Malkmus model (1967) avoids the underestimation of weak lines.

Calculations are performed in the new spectral regions defined from 1883 cm⁻¹ to 1917 cm⁻¹ for NO and from 1591 cm⁻¹ to 1607 cm⁻¹ for NO₂. Within these spectral regions, interference is caused by methane, nitrous oxide, water vapor, carbon dioxide, ozone and aerosol particles for NO, and by methane, nitrous oxide, water vapor and aerosols for NO₂. In this study the mixing ratios of the interfering gases

are from WMO (1985) and are assumed to be invariant with latitude, except for ozone. Calculations show that this approximation will introduce an error around 3% (mean value) for the calculated NO and NO₂ mixing ratios at sunset and sunrise. Temperature and pressure profiles are from the 1978 Air Force Standard Atmospheres and vary with latitude and season. Two km vertical resolution is assumed and the transmission values are calculated for NO and NO₂ and the interfering gases for the tangent paths. Retrievals can work downwards or upwards. The latter is better in controlling the effects of random noise at high altitudes. However, in this research study the retrieval starts from the highest altitude and works downwards for the following reasons:

- uncertainties in the NO and NO₂ mixing ratios at higher altitudes are smaller than at lower altitudes, mainly because of more accurate photodissociation rates and the slower variation of the concentration profiles.
- if the retrieval is from the bottom to the top and if the atmosphere is cloudy, instead of being cloudless as is generally assumed, any error arising from the presence of clouds will propagate upwards.
- effects for NO due to spatial/temporal variations along the ray path at sunset or sunrise are smaller at high altitudes than at low altitudes;
- in limb geometry most of the information is generally obtained at the tangent point because the absorber concentration is larger than in the layers above. However this is not the case for NO at sunset and sunrise because its mixing ratio increases rapidly with altitude.

The outline of a retrieval for NO or NO₂ follows:

- choose month and latitude;
- assign the temperature and pressure profiles for the particular latitude and month. Assign the set of NO₂ photodissociation rates and define whether the inversion is for sunrise or sunset;
- construct the mixing ratio profiles of NO or NO₂ for sunset or sunrise (hereafter assumed profiles) by using the photodissociation rates of NO₂, the temperature profile and the appropriate parameterization formula;
- calculate the transmission values using the Malkmus model for the tangent paths for NO or NO₂ and for the interfering gases;
- store the transmittances, define an initial guess mixing ratio for the top most layer and start the inversion for the concentration profiles of NO and NO₂;
- perform a number of iterations on transmittance until an a priori set convergence criterion (i.e., accepted maximum difference between the assumed and the retrieved profile) is satisfied;

- proceed to the next layer, using the mixing ratio in the previous layer as an initial guess;

6. Inversion Results

To test the accuracy of the inversion algorithm, the transmittances of nitric oxide and nitrogen dioxide and of the interfering gases are calculated for a variety of locations and seasons. Runs for selected cases are presented:

1. *Nitric Oxide*
 - a. July, 45°N, sunset
 - b. January, 30°N, sunset
 - c. January, equator, sunrise
2. *Nitrogen dioxide*
 - a. November, 60°N, sunset
 - b. January, 45°N, sunrise

The synthetic data for the transmittances are used to carry out the retrievals and to obtain the NO and NO₂ mixing ratios. The initial guess value at the highest levels for runs 1b and 2a is 7×10^9 molec/cm³, used to show convergence with poor initial value. For the remaining runs a better initial concentration of 7×10^8 molec/cm³ is chosen to speed the inversion procedures. The retrieved NO mixing ratio profile for 1a is shown in Figure 5(a, b) and in Figure 6(a, b) for run 1b.

The importance of a good initial guess profile can be seen comparing Figures 5(a), and 6(a). Retrieval 1b is characterized by a 5% error at the topmost layer. Such an error will affect the retrievals at the lower altitudes until approximately tangent altitude of 34 km where the increased NO number density smoothes out the error. Retrieval 1a starts with a good initial profile and gives a more accurate retrieved profile. Finally Figure 7(a,b) shows the NO profiles for run 1c, and Figures 8(a,b) and 9(a,b) show the retrieved NO₂ profiles for runs 2a and 2b, respectively.

Overall, NO₂ retrievals are more accurate than NO retrievals, the difference in accuracy being more pronounced at lower altitudes due to the smaller temporal and spatial variability of NO₂ compared to the variations of NO.

7. Conclusions

The inversion code provides results which satisfy accuracy expectations (within 5–15%), for both nitric oxide and nitrogen dioxide at sunset and sunrise over a wide range of geographic locations and seasons. Accuracies are for single profile retrievals and errors will be reduced for zonally averaged profiles or total column amounts. The algorithm's major advantage is that it effectively takes into account the interaction of photochemical and radiative processes. Therefore, by including the sunset and sunrise photochemistry of NO and NO₂ in the inversion procedures,

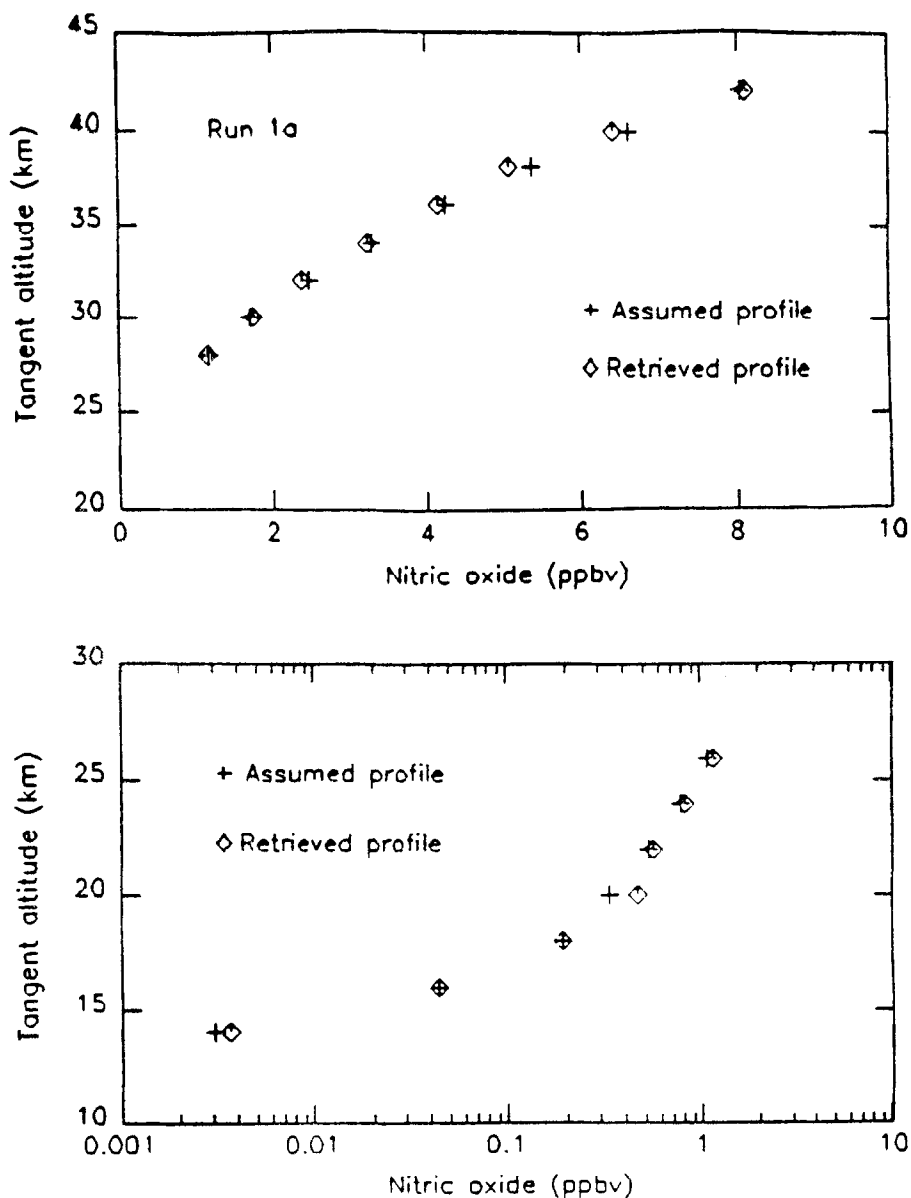


Fig. 5. NO retrieval at sunset (July, 45°N). (a) Higher range of altitudes. (b) Lower range of altitudes.

it eliminates the large errors which result if the temporal and spatial variations of the NO and NO₂ are neglected.

NO₂ retrievals are in general more accurate than NO retrievals for both sunset and sunrise. This can be attributed to the smaller temporal and spatial variability of nitrogen dioxide at sunset/sunrise and to the larger number density distribution of NO₂ at most altitudes.

NO₂ retrievals are more sensitive to errors and poor choice of an initial guess

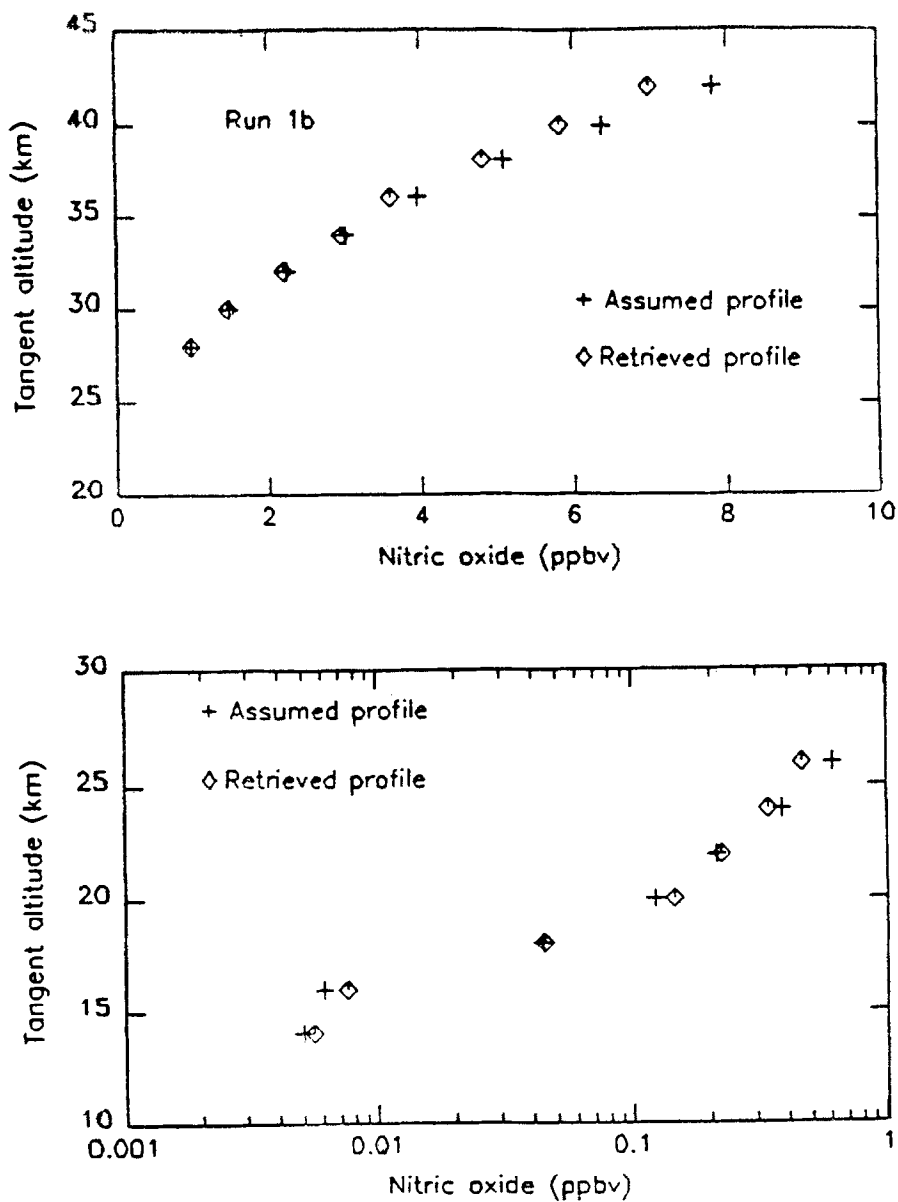


Fig. 6. NO retrieval at sunset (January, 30°N).

profile at the topmost layers (42 to 40 km). This is because NO_2 has smaller number density than NO at the layers from 42 to 40 km, and because at high altitudes NO_2 changes are directly proportional to NO changes and therefore more difficult to parameterize.

Sunset and sunrise retrievals are of the same accuracy for a cloudless atmosphere. The retrieval model works best if the atmosphere is cloudless, but if

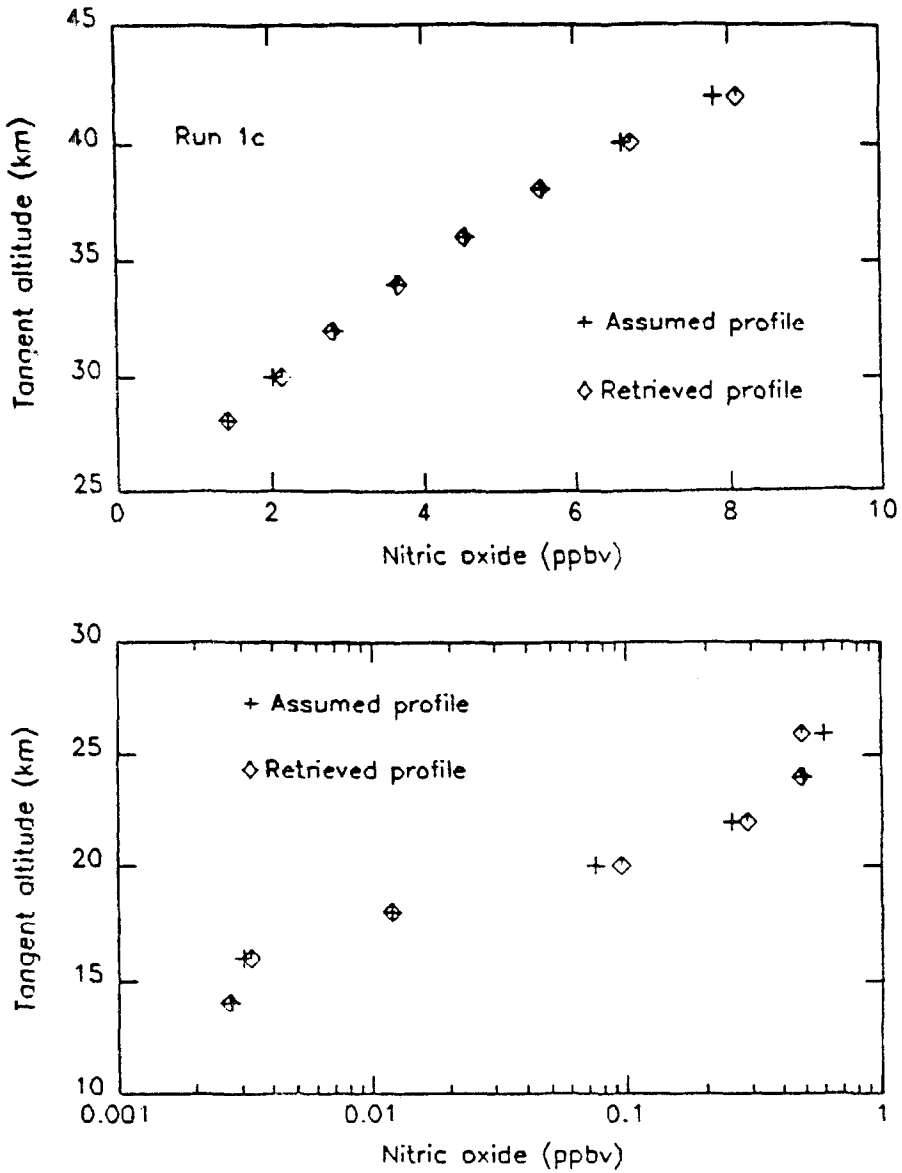


Fig. 7. NO retrieval for sunrise at the equator.

information on cloud coverage is available corrections can be applied for the mixing ratios below 20 km.

The performance of the model is tested by an extensive error analysis and it is found that errors are more important at low altitudes. This is a direct consequence of the increased temporal and spatial variability of NO and NO₂ at low altitudes where mixing ratios are as low as 0.003 and 0.1 ppbv for NO and NO₂ respectively.

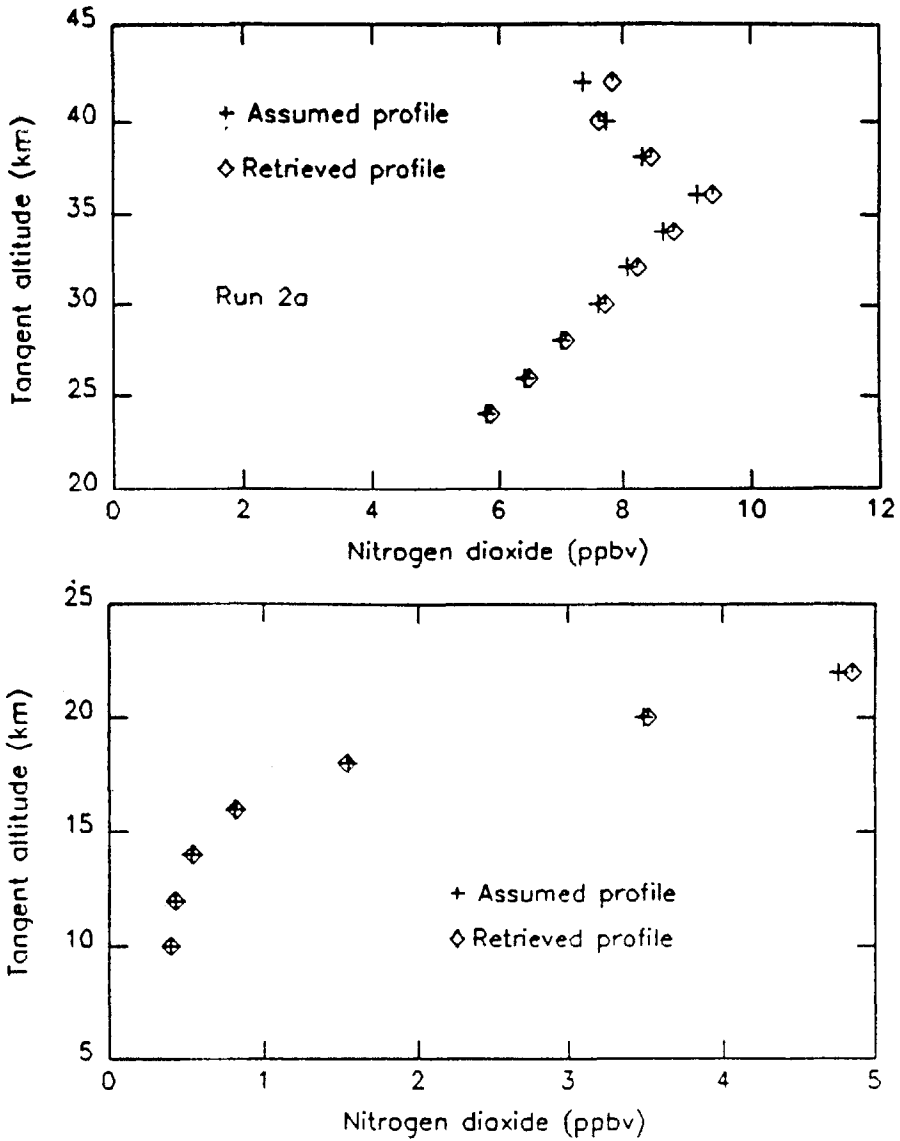


Fig. 8. NO₂ retrieval at sunset (November, 60°N).

The method is stable in the presence of most systematic and random errors but is sensitive to noise at low altitudes.

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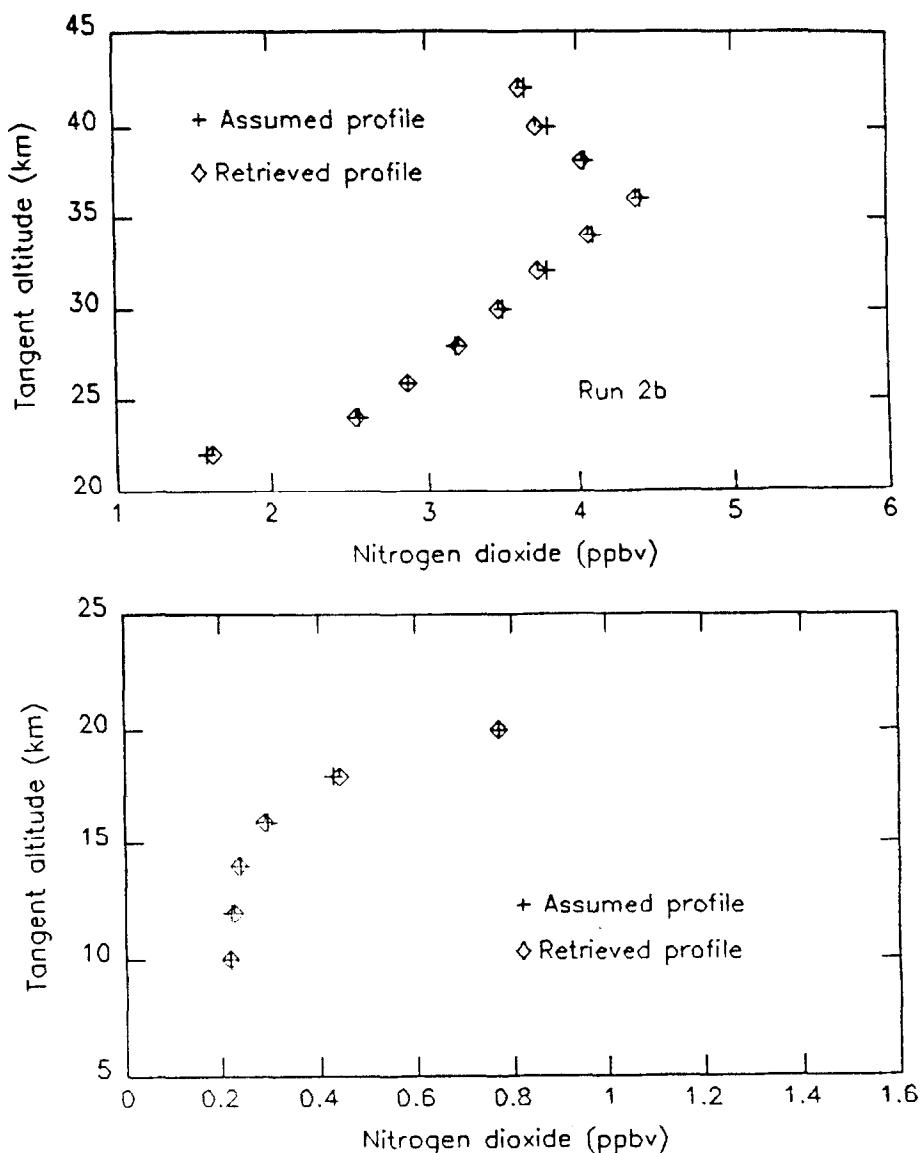


Fig. 9. NO₂ retrieval at sunrise (January, 45°N).

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