DIURNAL VARIATION OF STRATOSPHERIC NO AND NO₂ FROM MAP/GLOBUS 1985

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1. INTRODUCTION

The sum NO + NO_2 represents the major fraction of odd nitrogen in the mid-latitude stratosphere. The partitioning between NO and NO_2 is mainly determined by the photodissociation of NO_2 at wavelengths shorter than 405 nm:

$$NO_2 + h\nu \rightarrow NO + 0 \tag{1}$$

and by the catalytic cycle of ozone destruction:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2}$$
$$NO_2 + O \rightarrow NO + O_2 \tag{3}$$

Therefore, both species undergo large diurnal variations. At sunset, NO is rapidly converted into NO₂ as solar radiation is fading. During the night, NO₂ is partly converted into a reservoir species believed to be N_2O_5 , through the reactions :

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
 (4)

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$
 (5)

where M represents a third body. At sunrise, NO is rapidly re-formed from the photolysis of NO_2 and then, both NO and NO_2 slowly increases during the day because of the photodissociation of N_2O_5 .

This chemical scheme shows that NO, NO_2 and ozone are partners in very powerful temperature dependent photochemical reactions. Therefore, as pointed out by several authors (e.g. Roscoe et al., 1986; Solomon et al., 1986; McFarland et

al., 1986; Webster and May, 1987), the measurement of these species through a diurnal cycle is of particular importance in testing photochemical models.

A large set of data including NO, $\rm NO_2,$ ozone and temperature vertical profiles was obtained by various techniques from balloons, from satellites and from ground during the MAP/GLOBUS $\rm NO_X$ campaign of September 1985. The observations were performed at different local times in order to examine the diurnal cycle of NO and $\rm NO_2$ in the stratosphere.

In this paper, a subset of MAP/GLOBUS NO and NO_2 data taken at pressure levels of 18.1, 10.3 and 7.5 mb from balloons is compared to the predicted diurnal variation. The calculation is made with a time dependent zero dimensional model taking into account the current photochemistry. The model used observed ozone and temperature as fixed parameters.

2. OBSERVATIONS

The experimental NO and NO₂ data used in this work were obtained by different balloon borne instruments. All balloons were launched from the French Centre National d'Etudes Spatiales (CNES) base of Aire-sur-l'Adour ($43^{\circ}42'$ N, $0^{\circ}15'$ W). Table 1 summarizes the characteristics of each flight. Most of the experiments are described in earlier literature. The solar occultation technique at sunset (Pommereau et al., 1987) and the star occultation technique at night (Naudet et al., 1984) were used, in the visible spectral range, to obtain the vertical profile of NO₂. Note that three solar occultation instruments were set-up in the same gondola. Other instruments operated in the in situ mode. A matrix isolation cryosampler (Helten et al., 1984) was used to measure NO_2 during the day, and two chemiluminescent sondes (Fabian et al., 1987; Kondo et al., 1988) measured the mixing ratio of NO and its variation at sunrise and sunset.

Table 1 - Flight characteristics

DATE	TECHNIQUE	EXPERIMENTERS	
9/19	NO chemiluminescence	Y. Kondo W.A. Matthews	
9/19	NO ₂ visible solar occulation	J.P. Pommereau F. Goutail	
	NO ₂ visible solar occulation	P. Simon W. Peetermans	
	NO 2 visible solar occulation	N. Iwagami K. Shibasaki T. Ogawa	
9/20	NO chemiluminescence	P. Fabian	
9/24	NO 2 visible star occultation	J.P. Naudet P. Rigaud	
9/25	NO_2 matrix isolation	H. Helten	
10/4	NO chemiluminescence	Y. Kondo W.A. Matthews	

Ozone and temperature data are needed for model calculations. The vertical profile of ozone was measured during most of the flights listed in table 1. Additional ozone observations were made by satellite and ground-based experiments. Temperature profiles were derived from meteorological radiosondes, from lidar, from SSU measurements and from measurements made on certain scientific balloon gondolas.

3. MODEL

The calculation presented in this work were made using a time-dependent zero dimensional model (Ramaroson et al., 1987; Pirre et al., 1988) which is well adapted to study the diurnal variation of short lived species such as NO and NO₂. This model neglects dynamics and, therefore, the concentration of the long lived species must be fixed. Also the model includes full spherical geometry, Rayleigh scattering attenuation and mean albedo. The concentration of NO and NO₂ over a 24 hour cycle is calculated at each pressure level and for given ozone and temperature.

The long-lived species are H_2O , CH_4 , CO, H_2 , and the total amount of nitrogen species NO_y and chlorine species Cl_y . As these were not measured during the MAP/GLOBUS campaign, the mean values available from other observations (WMO, 1985)

Table 2 - Input for model calculations

PRESSURE (mb)	7.5	10.3	18.1
Tmax (K)	238.7	233.4	225.7
Tmin (K)	232.2	226.8	219.0
0 3 max (ppm)	8.6	8.1	6.9
03min (ppm)	7.1	6.5	5.4
NOy (ppb)	21.5	19.0	16.0

were used, except for NO_y that controls NO and NO_2 in the stratosphere. The amount of NO_y , was selected within the range of observations available from WMO (1985) so as to obtain the best agreement between the MAP/GLOBUS observations of NO_2 and the model. However, NO_y may change from day to day because of horizontal transport mechanisms. Therefore, it should be kept in mind that the model represents average conditions of NO_y while the observations may reflect sporadic dynamic effects.

Calculations were made at three pressure levels: 7.5, 10.3 and 18.1 mb that were selected as the best compromise between the number of avaiblable observations and the application range of the model. All available MAP/GLOBUS NO and NO₂ data taken at these levels within an interval of $\frac{1}{2}$ 0.5 mb are used in this work. Also for each level, maximum and minimum values of ozone and temperature as reported by Robbins (private communication, 1988) and Roscoe (private communication, 1988), respectively, were used in the calculations, in order to take into account the temporal variation of ozone and temperature during the MAP/GLOBUS campaign (Table 2).

4. COMPARISON

Figure 1 compares the mixing ratio of NO_2 observed at 7.5, 10.3 and 18.1 mb during MAP/GLOBUS with the corresponding modelled diurnal variation. The model calculations were performed for NO_y and both ozone and temperature values given in table 2, and for an albedo of 0.3. The solar occultation data result from the average of three observations made during the same flight (Table 1). Model and observations agree within error range, apart from the in situ observation made by Helten at 7.5 mb which is about a factor of three lower than the model.

Figure 2 is similar to Figure 1 but for NO mixing ratio. The accuracy of NO measurements is about 15 % (Fabian et al., 1987; Kondo et al., 1988). The values observed by Kondo in the morning at 18.1 and 10.3 mb compare favorably with the model. Other observations indicate that the mixing ratio of NO is larger than that predicted by the model. Also note that the discrepancy, between the model and the observations increases with altitude, and that the increase of NO observed during the day is larger than in the model.

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Fig. 1 : MAP/GLOBUS NO_2 mixing ratio compared to the diurnal variation calculated at 7.5, 10.3 and 18.1 mb using NO_y , ozone and temperature from table 2.

Fig. 2 : Similar to Fig. 1 but for NO.

Model calculations show that, for given NO_y , the changes in NO and NO_2 expected from the temporal variation of ozone and temperature during MAP/GLOBUS 1985 are not large enough to explain the daytime in situ observations. Minimum ozone and temperature lead to maximum NO_2 at night (reaction 4), and maximum NO during the day (reaction 2). Because of the equilibrium between NO and NO_2 (reactions 1 to 3), daytime NO_2 is not very sensitive to the ozone and temperature changes given in table 2.

Since the observations of NO and NO2 plotted in figures 1 and 2 were not made on the same day, dynamics may be responsible for day to day changes in $\rm NO_y$ leading to changes in NO and $\rm NO_2.$ However, it should be noted that very large changes in $\rm NO_y$ would be necessary to reconcile the model with both NO and $\rm NO_2$ from MAP/GLOBUS. For example, a value of NO_v as high as 30 ppb would be needed to fit the model to the NO values observed at 7.5 mb in the afternoon. It is also interesting to note that some of the in situ observations of NO and NO2 can be compared in terms of local time. For example, NO and NO2 was measured at 7.30 am by Fabian and around 7.00 am by Helten, respectively, for the same pressure level of 7.5 mb. Similar examples can be found at other pressure levels, and the sum of these observations has been plotted on Figure 3 along with the predicted diurnal variation of NO + NO_2 . The nightime value is identical to the NO2 mixing ratio measured by star occultation (see fig. 1), since NO is entirely converted into NO2 at sunset. The daytime values derived from the in situ observations of NO and NO2 compare favorably with the model. Also note that the differences between observations and model seen in Figures 1 and 2 at 7.5 mb tend to cancel each other. Considering that NO + NO2 directly depends on NO_y and that the model calculations were made using a constant value of $\rm NO_y$ (table 2), the good agreement seen in Figure 3 suggests that no large variation in NO_v occured during the MAP/GLOBUS campaign.

If dynamics cannot explain the discrepancy between in situ observations and model, Figure 1 to 3 indicate that the partitioning between NO and NO2 differs significantly from that in the model. The balance between NO and NO2 in the sunlit atmosphere is strongly dependent on the visible radiation field via the photodissociation of NO₂ (equation 1). The photodissociation coefficient J_{NO_2} is a complex function of solar zenith angle and albedo, involving multiple scattering effects (Madronich et al., 1985). The model used in this work takes into account albedo effects but multiple scattering is neglected. Therefore, it is interesting to test the validity of this approximation against direct observations of J_{NO_2} , and also to evaluate the sensitivity of the calculated ratio NO/NO2 to change in albedo. Figure 4 compares the $J_{\rm NO2}^{-}$ calculated by the model using an albedo of 0.3 with the measurements from Madronich et al. (1985). The good agreement seen on this figure, indicates that the model uses realistic values of $J_{\rm NO_2}.$ An average albedo of 0.3 was selected for the present work, because all balloon flights were made over land during clear sky periods. However the diurnal variation of NO and NO2 has been re-calculated using a value of 0.6 an overestimate since no clouds were present during the observations. Such an albedo would increase the calculated mixing ratio of NO and decrease that of NO_2 by less than



Fig. 3 : Similar to Fig. 1 but for NO + NO_2 .

11 %. Therefore changes in albedo cannot explain the difference seen in Figure 1 and 2 between model and in situ observations.



Fig. 4 : Photodissociation coefficient of NO_2 versus solar zenith angle, as observed at 32 km by Madronich et al. (1985) and as calculated by the model using an albedo of 0.3.

Kondo et al. (1988) measured the decay of NO toward sunset during the flight of September 19. They compared the relative variation of NO as a function of solar zenith angle with a simplified calculation based on the photochemical equilibrium between NO and NO2. Good agreement was found between calculation and observations, but the comparison was limited to solar zenith angles smaller than 90°. Figure 5 extends the comparison toward larger zenith angles using the model of Pirre and Ramaroson. Observations were taken at about 31 km, and the reference value NO day corresponds to that measured at the begining of the afternoon (Kondo et al., 1988). Model calculations were made for 10.3 mb (\approx 31 km) using NO_y , ozone and temperature from table 2. The model generally agrees with the observations. In particular, the model shows the decrease of NO observed during the afternoon. However, a small



Fig. 5 : NO mixing ratio relative to its daytime value (NO_{day}) versus solar zenith angle, as observed at sunset by Kondo et al. (1988), compared to model calculations using NO_y, ozone and temperature from table 2.

difference between observed and calculated values appears at a zenith angle of 85°, reaching a maximum of 35 % at 91° and then decreasing for larger zenith angles. This suggests that the sunset conversion of NO into NO₂ begins earlier than predicted by the model. Similarly, by using LIMS NO₂ data, Solomon et al. (1986) have shown that, below 5 mb, the buildup of NO₂ at sunset begins earlier than 90°. These authors have concluded that models should take into account multiple scattering processes to fit the observations better. Therefore, as multiple scattering is neglected in the present work, the slight disagreement seen in Figure 5 may partly reflect the solar zenith angle dependence of multiple scattering processes.

5. CONCLUSION

The diurnal variation of NO and NO2 at 18.1, 10.3 and 7.5 mb have been derived from MAP/GLOBUS data, and compared with a time-dependent zero dimensional model. The model agrees with the observations of NO_2 apart from the in situ observation at 7.5 mb which is lower than the The model also the agrees with model. observations of NO made by Kondo in the morning, but yields lower values than those observed by Fabian in the morning, and by Kondo in the afternoon. These differences between the model and the daytime in situ observations of NO and NO2 indicates that the calculated partitioning between NO and NO_2 differs from that observed. The examination of the sum NO + NO_2 suggests that no large variation of the total amount of nitrogen species occured at 18.1 mb and above during the MAP/GLOBUS campaign and, therefore, that the comparison presented in this paper is not strongly affected by dynamical processes. It is also shown that the relative variation of NO through sunset favorably compares with the model. Further model calculations should include other multiple scattering processes. Also MAP/GLOBUS observations that are not yet available, such as, for example, the daytime observations of $\rm NO_2$ by SME would further refine this work.

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