

MEASUREMENTS OF NITRIC OXIDE DURING A STRATOSPHERIC WARMING

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Abstract. The altitude distribution of NO was measured between 12 and 33 km near 54°N during the stratospheric warming of February, 1979. The NO mixing ratios were considerably smaller compared to summer conditions, especially below 23 km. The measurements are used to estimate the distribution of NO₂ for comparison with ground-based column measurements and to show that during the warming NO_x is at least a factor of two lower than is observed in summer at this latitude. This reduction in NO_x is shown to be consistent with a larger fraction of odd-nitrogen existing as N₂O₅.

Introduction

The stratospheric warming of January and February 1979 has been the subject of several recent studies. Quiroz (1979) has analyzed the physical properties of the warming. Hilsenrath (1980) has reported several rocket ozone-sonde profiles. Noxon et al. (1979, 1980) have reported ground-based measurements of stratospheric NO₂ in a portion of the normally zonal polar vortex flow that was displaced well south of its usual location over the pole. Here a measurement of the altitude distribution of NO obtained during the warming is reported. This occurred fortuitously as part of a three year program (1977-1979) to investigate seasonal changes in odd-nitrogen species at northern latitudes. The York University balloon payload was launched from Canadian Forces Base, Cold Lake, Alberta (110°W, 54.4°N) on Feb. 11/79 at 1306 LT (2006 Z). Measurements of NO were obtained with a chemiluminescence instrument that has been described elsewhere (Ridley and Schiff, 1981).

A scanning radiometer for measurements of HNO₃, operated by the Atmospheric Environment Service (AES), was included in the payload. Results from that instrument and ground-based measurements of NO₂ are reported by Evans et al. (1982).

Observations

The NO mixing ratios measured on ascent and during the float period are shown in Figs. 1 and 2. Included in Fig. 1, for comparison, is an average of several summer profiles measured near this latitude (Ridley and Hastie, 1981). The winter mixing ratios are smaller at all altitudes but particularly in the low to mid-stratosphere where from 12 to 18 km, at 20 km and at 23 km they are 2-3, 4 and 6 times lower than in summer, respectively. This difference would be amplified if the data were plotted relative to the respec-

tive tropopause altitudes. Although the present measurements were made during a warming, the winter profile bears a qualitative resemblance to those obtained from the same location in February 1977 and 1978. A comparison of the three winter profiles will be presented elsewhere, but common features show low NO compared to summer below 23-26 km accompanied by a rapid increase to values comparable to those of summer in the 29-33 km region. However, the onset of this rapid increase varied from year to year and in 1977 there was a peak near 14 km.

Figs. 3 and 4 present a temperature profile and O₃ mixing ratios measured by the AES. The extent of the warming is illustrated by a comparison of the 1979 temperature profile with one from the 1978 campaign, a normal winter profile, and with one from summer at 51°N (Ridley and Hastie, 1981). In contrast, the winter mixing ratios of O₃ are similar except for structure near 14 km and lower mixing ratios above 29 km in 1979. As expected, both winter profiles exhibit much larger mixing ratios in the lower stratosphere compared to summer conditions.

Discussion

The time constant for daytime partitioning of NO_x (NO + NO₂) is only a few minutes so that trans-

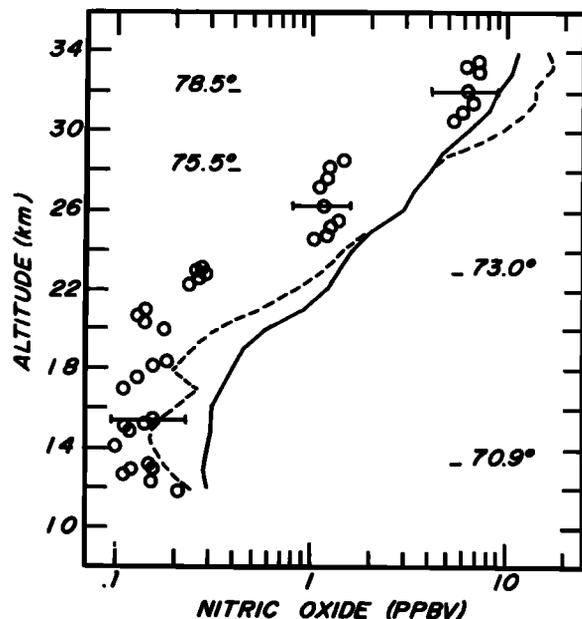


Fig. 1. The mixing ratio of nitric oxide measured on ascent (open circles). The solar zenith angle (χ) is indicated to the right and left of the data. The solid line is the average NO from several summer flights near this latitude. The dashed curve is described in the text.

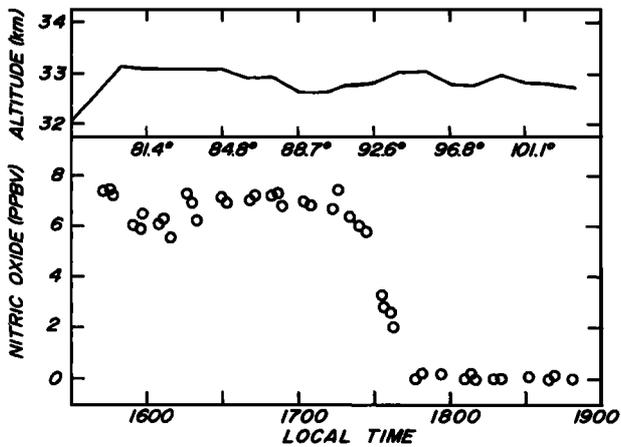


Fig. 2. The decay of NO during sunset. The solar zenith angle was calculated for the balloon position.

port processes may be ignored. Changes in the partitioning between summer and winter warming conditions can then be examined on the basis of differences in insolation, temperature, and the abundance of O_3 . In winter, decreased insolation and increased O_3 densities below about 23 km favour larger amounts of NO_2 . The higher temperatures at lower altitudes during the warming amplify this tendency to NO_2 .

These effects can be examined quantitatively if it is assumed that NO_x is conserved between the summer season and the winter warming period. The average summer NO profile of Fig. 1 was used to compute NO_x for the summer conditions of temperature and O_3 assuming the usual photochemical steady-state relation for the NO_2/NO ratio (cf. Ridley and Hastie, 1981). The photodissociation coefficient of NO_2 was calculated using a multiple scattering routine and a 25% surface albedo (Madronich et al., 1982). This calculated summer NO_x was then subjected to the winter warming insolation, temperature and O_3 conditions of Feb. 11/79. The calculated winter NO, shown as the dashed curve of Fig. 1, approaches that measured at the lowest altitudes mainly due to increased O_3 oxidation in winter but is still significantly larger than was observed at higher altitudes. Furthermore, the calculated winter NO_2 , corresponding in time to the dashed curve of Fig. 1, yields a column amount of $5.5 \times 10^{15} \text{ cm}^{-2}$. This daytime NO_2 column is about twice that measured by the AES at evening twilight at the launch site (Evans et al., 1982) and also about twice as large as would be interpolated from evening measurements of $4 \times 10^{15} \text{ cm}^{-2}$ at 50°N and $2 \times 10^{15} \text{ cm}^{-2}$ at 65°N reported by Noxon (1979, 1980) for a warming event in Jan. 1978 when the stratospheric flow pattern was similar to that prior to the present balloon flight. Thus the winter warming NO profile is not solely a reflection of differences in NO_x partitioning but indicates a substantial reduction in NO_x from summer to winter warming conditions.

The magnitude of the winter warming reduction in NO_x can be examined in more detail if the measured NO profile is used to estimate the abundance of NO_2 during the warming. This also allows a comparison to be made between ground-

based measurements of the column abundance of NO_2 and that inferred from the observed NO profile.

Fig. 5 presents the NO_2 profile, corresponding in time to the measured NO, calculated as described above from the steady-state NO_2/NO ratio using the measured O_3 and temperature distributions of the warming. A comparison with ground-based measurements requires the conversion of this mid afternoon profile to that for twilight conditions. Evening NO_2 was estimated by summing daytime measured NO and calculated NO_2 and partitioning this according to the photodissociation coefficient at $\chi = 90^\circ$. As the photodissociation of ambient N_2O_5 is very slow, the small release of NO_x from N_2O_5 during the late afternoon was neglected. Morning twilight NO_2 was estimated by incorporating the expected formation of N_2O_5 during the long night and partitioning the remaining NO_x for $\chi = 90^\circ$ in the morning. The estimated column densities of NO_2 for morning twilight, mid afternoon and evening twilight are in units of 10^{15} cm^{-2} , 1.2, 2.7 and 3.0, respectively. The twilight estimates are in good agreement with those reported for the balloon campaign by Evans et al. (1982), those of Syed and Harrison (1981) for Calgary, some 450 km south west of Cold Lake and those of Noxon (1979, 1980) for the 1978 warming referred to earlier. The daytime winter warming NO_x column abundance is then $\sim 5 \times 10^{15} \text{ cm}^{-2}$ (NO : $2 \times 10^{15} \text{ cm}^{-2}$; NO_2 : $2.7 \times 10^{15} \text{ cm}^{-2}$). In summer at these latitudes a typical value is $\sim 11 \times 10^{15} \text{ cm}^{-2}$ (NO : $4.5 \times 10^{15} \text{ cm}^{-2}$, Ridley and Hastie, 1981; NO_2 : $6 \times 10^{15} \text{ cm}^{-2}$, Evans et al., 1982). Thus NO_x during the warming remained at least a factor of two below that observed in summer.

The seasonal difference in the abundance of

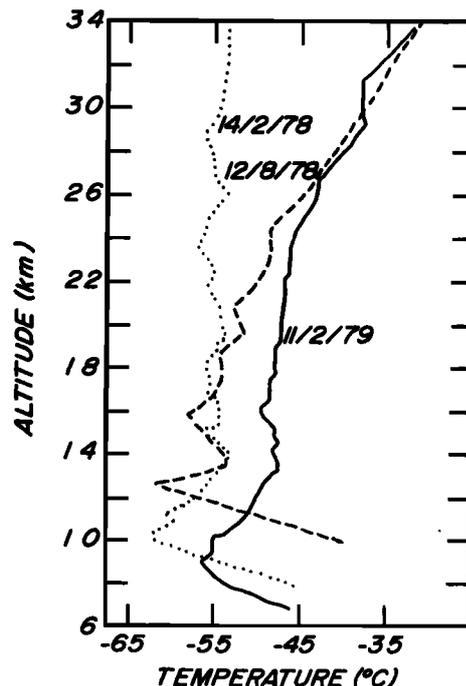


Fig. 3. A comparison of the atmospheric temperature profile for the present flight with one for summer near this latitude and with one obtained during a balloon flight on Feb. 14/78 when no warming was present.

NO_x at northern latitudes may result from a combination of transport and conversion to a winter storage reservoir. Current chemistry suggests that HNO₃, HNO₄ and N₂O₅ are possible reservoirs and Evans et al. (1982) use their measurements of HNO₃ to examine the suggestion by Noxon et al. (1979) that HNO₃ is the principal reservoir. On the other hand, N₂O₅ chemistry alone can account for both the diurnal change in NO₂ and the reduction in NO_x during a warming. At 54°N in winter, the diurnally averaged photodissociation lifetime of N₂O₅ is about 3 days. Thus the long winter nights, the high O₃ densities in the lower stratosphere and the higher temperatures should combine to increase the fraction of odd-nitrogen that is present as N₂O₅ compared to summer conditions if an air mass spends only a few days near or north of the latitude of Cold Lake. This would be anticipated even if the air mass originated from latitudes south of Cold Lake.

The stratospheric circulation during the warming was unstable and so it is difficult to accurately determine the time the air mass sampled during the balloon flight resided near or north of Cold Lake. Upper air charts indicated that Cold Lake was near the edge of the flow about the polar low pressure region below about 22 km for several days prior to the flight. At higher altitudes and for several days prior to the flight the polar low was distorted by a high pressure region over Alaska and it is possible that the sampled air originated in part from latitudes south of 50°N and west of the high pressure region. However, the clockwise flow west of the high towards the pole was quite weak. Eastward of the high, the flow southwards towards Cold Lake was weaker still. Consequently, the transit time for flow from 50°N poleward about the high to 65-70°N and southward to Cold Lake was estimated at just over 4 days. Thus, even if the air mass followed

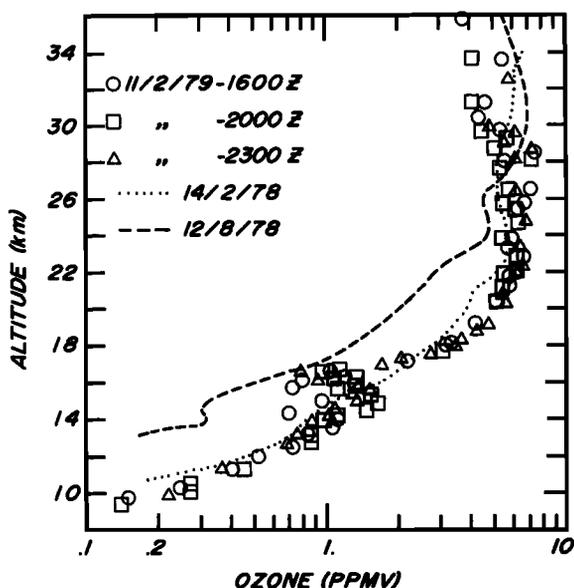


Fig. 4. A comparison of the ozone mixing ratio from three sondes launched by the AES on the day of the balloon flight with that obtained on previous flights as described in Fig. 3.

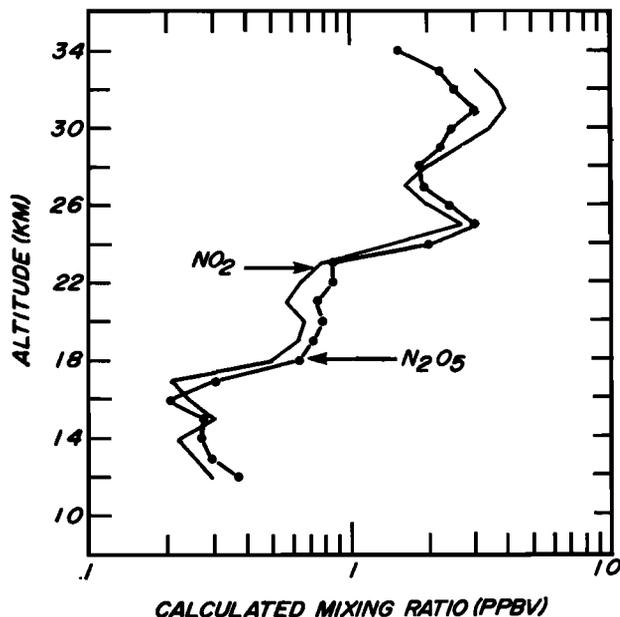


Fig. 5. Estimated steady-state mixing ratios of NO₂ and N₂O₅ derived from the winter NO profile.

this route alone, a large conversion of NO_x to N₂O₅ would be anticipated.

The expected steady-state abundance of N₂O₅ is given in Fig. 5. This was estimated by determining the N₂O₅/NO ratio from a one-dimensional diurnal model (J.C. McConnell, private communication) run for the flight conditions of O₃ temperature and the time of the measured NO. The N₂O₅ distribution of Fig. 5 yields a column abundance for the afternoon of 2.9 x 10¹⁵ cm⁻², comparable to that of evening NO₂. Combining this with measured column NO and calculated afternoon column NO₂ yields an NO_x + 2N₂O₅ daytime abundance of ~ 11 x 10¹⁵ cm⁻². A typical value for summer conditions near this latitude is 13 x 10¹⁵ cm⁻² derived using the previous estimate of summer NO_x and taking N₂O₅ as 1.2 x 10¹⁵ cm⁻² from similar model calculations. Within these estimates it would appear that current model chemistry can account for the seasonal change in NO_x and the observed diurnal change in NO₂. This, of course, does not rule out the possibility of slow conversion of NO_x to HNO₃ during long term and stable polar circulation conditions.

An N₂O₅ reservoir is also consistent with Noxon's constraint (1979) that the winter reservoir must release NO_x photolytically upon transport to lower latitudes. An upper limit for the column abundance of N₂O₅ above 18 km of 2 x 10¹⁴ cm⁻² has been reported by Murcray et al. (1978) for 57°N in February 1978. This limit is more than a factor of 10 below our estimate and if it should survive measurements designed specifically to measure N₂O₅ then the storage reservoir(s) remains to be identified. HNO₃ cannot explain the observed diurnal variation in NO₂ column abundance and so cannot be the only reservoir species. HNO₄ has a photolysis time constant similar to that for N₂O₅ but current models estimate too small an abundance to account for the magnitude of the diurnal change.

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