Stratospheric Odd-Nitrogen: NO Measurements at 51°N in Summer

B. A. RIDLEY AND D. R. HASTIE

Department of Chemistry, York University, Downsview, Ontario M3J 1P3

The altitude distribution of nitric oxide was measured during three balloon flights in August 1976 and 1978. Median values of the volume mixing ratio at 18, 24, 30, and 34 km were 0.4, 1.4, 6.5, and 13 ppb, respectively. The data are discussed in relation to an average profile of nitrogen dioxide measured for this season and latitude and in relation to current one-dimensional models of the stratosphere.

INTRODUCTION

During the summers of 1974–1978, balloon flights have been conducted either independently of or jointly with the Atmospheric Environment Service of Canada (AES) to obtain measurements of trace species in the stratosphere at 51°–59°N. A principal aim of the AES project Stratoprobe flights was to obtain simultaneous altitude distributions of the principal odd-nitrogen species $NO(\equiv NO_2 + NO + HNO_3)$. *Evans et al.* [1976, 1977, 1978; see *National Academy of Sciences*, 1979] have found that profile measurements of NO_2 and HNO_3 obtained by long-path techniques were remarkably similar during all these flights which were made under substantially similar conditions of stratospheric O_3, temperature, and circulation. In contrast, in situ measurements of NO [*Ridley et al.*, 1976; *Evans et al.*, 1978] sometimes exhibited considerable differences in the altitude profiles. Although considerable variability in NO distribution in the stratosphere seems to be an accepted occurrence [e.g., *National Academy of Sciences*, 1979; *Hudson*, 1979], gross changes in the abundance of NO for conditions where O_3, temperature, NO_2, and HNO_3 are invariant would seem implausible. In fact, our observations of gross changes in stratospheric NO prompted a reexamination of the air sampling and calibration technique employed. As has been discussed by *Ridley and Schiff* [1981], it is likely that some measurements of NO reported earlier from this laboratory underestimate the actual abundance of NO. However, the nature of the problem identified in that paper was such that it is impossible to distinguish which of or by how much the earlier measurements are in error.

In this paper, measurements of NO obtained by using improved air sampling and in situ calibration are presented. It is suggested that these and some earlier measurements are typical of summer conditions at 51°N. The results are discussed in relation to measurements of nitrogen dioxide reported by the AES and are also compared to predictions from stratospheric models that are used to estimate possible ozone changes in the atmosphere owing to human activity. These models have been recently reviewed and summarized in the *Hudson* [1979] report.

EXPERIMENTAL

The NO volume mixing ratio was measured with a chemiluminescence instrument that has been described previously [*Ridley et al.*, 1977; *Ridley and Schiff*, 1981]. Two flights were made in conjunction with the AES from Yorkton, Saskatchewan (51.3°N, 102.8°W), in August 1976 to obtain simultaneous measurements of HNO_3, NO_2, and NO. Another flight of the NO instrument was made from the same location in Au-

gust 1978. For the 1976 flights the AES also made extensive measurements of O_3, using both a Dobson instrument and Mast-Brewer sondes. Those data have been reported by *Evans et al.* [1979]. For the 1978 flight, 11 EEC ozonesondes were flown between August 10 and 24. The NO results for both years are given in Figures 1–3, together with the O_3 volume mixing ratio obtained from several sondes launched to span the time of the odd-nitrogen balloon payload. Corresponding temperature data are given in Figure 4.

Ridley and Schiff [1981] have described a modification of the air sampling and in-flight calibration procedure that minimizes sampling errors that have likely occurred on some of the earlier flights. This modification was made prior to the flight in 1978 but not for the two flights in 1976. Thus we have more confidence in the data obtained in 1978. However, the overall agreement between the measurements in the 2 years for very similar atmospheric conditions also lends confidence to the validity of the data obtained in 1976, because the sampling problem discussed in *Ridley and Schiff* [1981] would always tend to underestimate atmospheric NO. Clearly, it is impossible to assess measurement uncertainties for the 1976 profiles, but they are certainly no less than the ±30% uncertainty estimates for the data of August 12, 1978, which are given in Figure 3. A discussion of the known sources of possible error in the measurements has been given by *Ridley and Schiff* [1981].

There remains a proviso concerning the flight of August 19, 1976. Upon launch, the 3×10^{15} m^3 balloon suffered a large tear near the bottom that was observed to allow entrainment of a considerable quantity of near-surface air likely rich in $NO_x (\equiv NO + NO_2)$ from support and launch vehicle exhausts. Consequently, expulsion of this trapped air as the balloon ascended may have perturbed the ascent data. Certainly, the observed mixing ratio of NO in the 18- to 20-km region is much larger than observed on the other two flights. Whether this is due to atypical dynamics in the stratosphere or to expelled air is speculative. Nevertheless, the reasonable agreement between the ascent and descent data suggests that possible contamination of the payload (~80 m below the balloon) was insignificant at higher altitudes or at later times.

DISCUSSION

Evans et al. [1977, 1978, 1979] have reported that total column O_3 and temperature were similar for flights made from Yorkton in 1975 and in 1976. In 1976, total O_3 for 3 days spanning August 19 and 28 were 291 ± 3 and 309 ± 13 matm-cm, respectively. In 1978, the sondes flown gave a value of 302 ± 11 matm-cm. It is evident from Figures 1–4 that above about 15 km the distributions of O_3 and temperatures are also comparable for the 2 years. At lower altitudes the variations
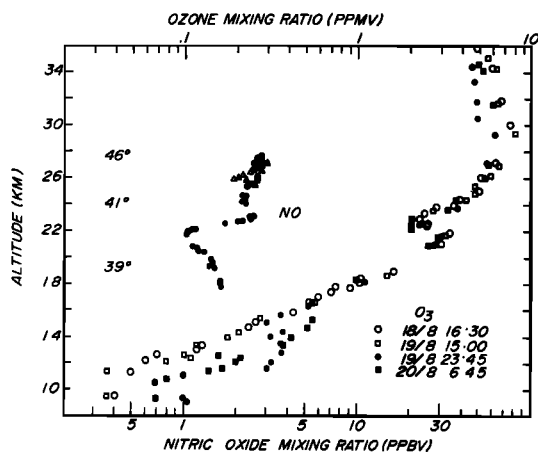
Fig. 1.   NO (lower scale) and O_3 (upper scale) volume mixing ratios for the flight of August 19, 1976. Launch time: 1200 LT (1800 GMT) Times for ozone measurements are GMT. NO: Solid circle indicates ascent data; open triangle, descent data. The solar zenith angle during ascent is indicated.

reflect changes in the height of the tropopause. An exception to the similarity of the O_3 profiles for the 2 years is that the persistent 'notch' near 22.5 km observed in 1976 and described by Evans et al. [1979] is not obvious in the 1978 profiles. Instead, it is not clear whether a slight peak near 24 km or a weak notch near 26 km exists in the 1978 mixing ratio profiles. Nevertheless, the gross features of the in situ O_3 and temperature distributions and of the long-path measurements of NO_2 and HNO_3 [Evans et al., 1977, 1978; McElroy and Kerr, 1979; Evans and O'Brien, 1979] are quite similar for all the summer flights made from Yorkton by the AES. Consequently, similar abundances of NO would be anticipated for the 2 years, and this is substantiated by the overall similarity of the data given in Figures 1-3. We can only conclude that the mixing ratios of NO determined from flights near Churchill in 1974 [Ridley et al., 1976] and from Yorkton in 1975 shown in Ridley and Schiff [1981] underestimate the actual NO abundance owing to the sampling and calibration problems mentioned previously.

The NO measurements shown in Figures 1-3 were made at different times of the day so that any intercomparison of them must consider the expected daytime variation. N_2O_5 formed during the night is photolyzed during the morning to produce
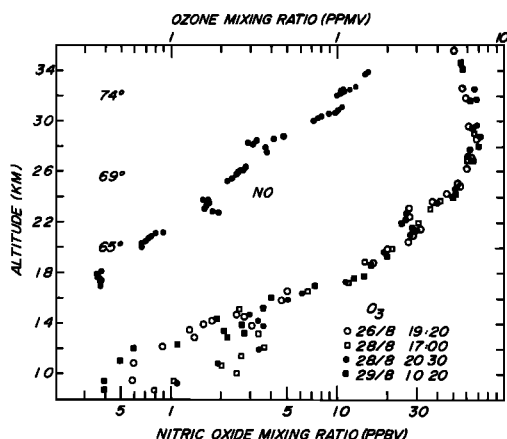
NO_x. Since the quantum yield for N_2O_5 photodissociation is not known, it is not possible to calculate accurately the rate at which this temporary reservoir is converted to active NO_x. However, the quantum yield is usually assumed to be unity, and models at 30°N at equinox typically estimate about a 25% increase in NO in the 20- to 25-km region as the solar zenith angle (χ) decreases from 50° to 30° in the morning compared to only 10% from noon to $\chi = 75°$ (J. Chang, private communication, 1979). For the measurements reported here, χ changed from about 50° through 36° at noon to about 75° in the afternoon, and thus an intercomparison of the three profiles should not be greatly perturbed by differences in the time of measurement. Certainly, the observation that during the August 12, 1978, flight the descent measurements are higher on average is consistent with the change in zenith angle, but it also must be remembered that different air masses are sampled on ascent and descent. For the present purposes it is reasonable to consider the measured NO profiles as representative of high sun conditions.

The O_3 and NO distributions were not measured exactly simultaneously, so that a detailed comparison of structure in the profiles is not meaningful. However, there are rather persistent features in the O_3 profiles, and it is interesting to note that there is a hint of a local maximum in NO for both flights in 1976 at the altitude of the O_3 notch referred to earlier. There is also an indication of a local minimum in the NO descent data near 24 km where there appears to be a weak O_3 mixing ratio maximum in 1978. Thus there is some evidence for an anticorrelation between NO and O_3 which would be expected for air volumes that contained the same NO_x but different O_3 abundances. But if these persistent features in O_3 are due to transport of air from different source regions, then an anticorrelation between O_3 and NO need not be expected.

In spite of these differences in detail, it is suggested that the NO mixing ratio profiles of August 12, 1978, and August 28, 1976, are typical of the lower and middle stratosphere for this latitude and season. For the discussion to follow the envelope of these two distributions is given in Figure 5, and the median of this envelope is used in calculations. Because of the possible problem associated with the August 19, 1976, flight, those data have not been used further, although inclusion of the higher altitude data would not change the calculations or conclusions.

Fig. 2.   Same as for Figure 1. NO measured on ascent during afternoon of August 28, 1976. Launch time: 1550 LT (2150 GMT).
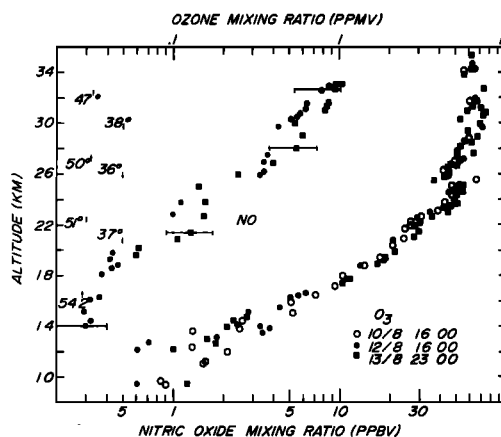

Fig. 3.   Same as for Figure 1. NO: open circle indicates ascent; solid square, descent data for the flight of August 12, 1978. Launch time: 0845 LT (1445 GMT).

Comparison With Other Measurements

Direct support for the suggestion that the envelope of Figure 5 is typical of NO in summer at 51°N is provided by a comparison with the measurements of *Loewenstein et al.* [1978] made from a U-2 aircraft. They have made extensive latitudinal surveys of NO in the 18- to 21-km region, using a chemiluminescence instrument of similar design to that used here. Our data are in good agreement with the range and average measured, using the U-2 for this season and latitude as shown in Figure 5.

Further support for the suggestion made above results from a comparison of the NO data with the average of NO_2 measurements obtained over several years at Yorkton by McElroy, Kerr, and Evans [*Evans et al.*, 1978; see also *National Academy of Sciences*, 1979]. Some of the NO_2 data used to formulate this average were obtained on the same balloon flight as the NO measurements in 1976. The daytime NO_2/NO interconversion is rapid throughout the stratosphere, and the ratio should, in terms of present chemistry, be given by the photochemical steady state expression

$$\frac{[NO_2]}{[NO]} = \frac{k_{NO/O_3}[O_3] + k_{ClO/NO}[ClO] + k_{NO/HO_2}[HO_2]}{J_{NO_2} + k_{O/NO_2}[O]} \quad (1)$$

J_{NO_2} is the photodissociation coefficient of NO_2 and the k's are the rate coefficients for the reaction between the species indicated. The first term in each of the denominator and numerator of (1) are dominant in the altitude region of interest here. Expression (1) was evaluated at 2 km intervals, using (1) the average of O_3 and temperature data for the 1976 and 1978 flights; (2) the average of the fall ClO measurements of *Anderson et al.* [1980]; (3) neglecting the minor term involving O atoms and HO_2 radicals; (4) calculating J_{NO_2} according to the method described by *Isaksen et al.* [1977], using an albedo of 0.25. In the calculation of J_{NO_2}, the solar flux values of *Ackerman* [1971], the low temperature absorption coefficients listed in *Hudson* [1979], and the low temperature quantum yields of *Davenport* [1978] and those of *Harker et al.* [1977] were used. A possible uncertainty of ±20% was assigned to J_{NO_2} to allow for uncertainty in the above parameters and, more importantly, for uncertainties in the treatment of multiple scattering and albedo.

The calculated NO_2/NO range is given in Figure 6. Also

Fig. 5. A comparison of the range of NO measurements of August 12, 1978, August 28, 1976 (cross-hatched region) with the one-dimensional model range (shaded region) from *Hudson* [1979]. The ozone profile range is also compared to that from one of these models, viz. solid circle, J. Chang (private communication, 1980). The average and range of NO measurements by *Loewenstein* [1978] for 51°N are indicated by the thin rectangles.

shown is the observed NO_2/NO ratio determined from the median of the NO data and a median NO_2 determined by using two methods. In the first method, since the evening twilight determinations of NO_2 by McElroy, Kerr and Evans [see *National Academy of Sciences*, 1979] are strongly weighted to $\chi = 90°$ the profile was converted to one at $\chi = 50°$, more appropriate to the time of the NO data, using factors $NO_2(\chi = 90°)/NO_2(\chi = 50°)$ from the diurnal model of J. Chang (private communication, 1979). These factors were 0.47, 0.65, 0.79, and 0.78 at 14, 20, 26, and 32 km, respectively. In the second method, a model independent 'daytime' NO_2 profile was determined simply by averaging the morning and evening twilight NO_2 data. Above about 23 km, the 'observed' NO_2/NO ratios obtained by the two methods are in reasonable agreement with that calculated from (1). At lower altitudes the model corrected observed ratio is almost a factor of 2
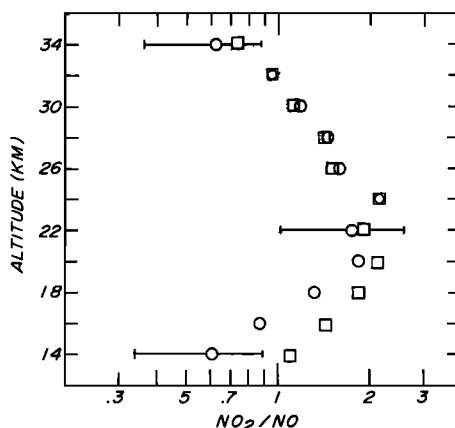
Fig. 6. A comparison of the photochemical steady state NO_2/NO ratio (shaded region) with that based on the average of the NO data reported here and the average of the NO_2 data of McElroy and Kerr [see *National Academy of Sciences*, 1979]. The open circle indicates the observed ratio using model corrected NO_2 evening twilight data [see text]. The estimated uncertainty is given at 14, 22, and 34 km. Open square, observed ratio using the average of morning and evening twilight NO_2 data. The shaded region is the calculated NO_2/NO ratio allowing ± 20% uncertainty in J_{NO_2}.
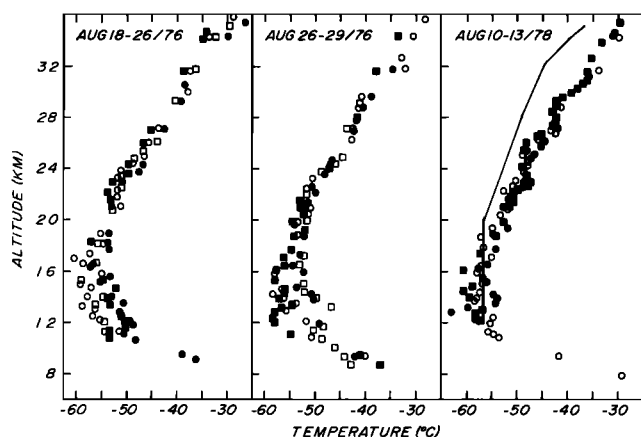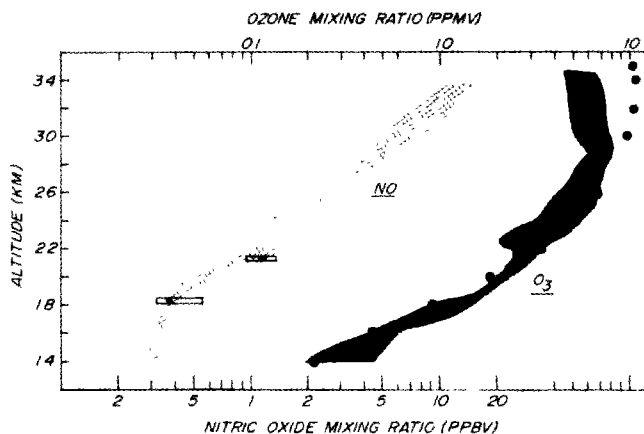

Fig. 4. Temperature profiles corresponding to the ozonesonde flights of Figures 1–3. The solid line indicated on the August 1978 data is from the model of J. Chang (private communication, 1979).

larger than the central value determined from (1), while the simple average observed ratio is up to a factor of 3 larger. This latter discrepancy is larger than the combined estimated uncertainty in the observed and calculated ratio shown in Figure 6, but the calculated ratio range does not include the uncertainty in k_{NO/O_3} or in the measurements of O_3 and temperature. Although the comparison is made between in situ and long-path techniques, the observed ratio is derived from averaging data over several years, and this should compensate to some extent the fact that the measurements are made in different air masses. Nevertheless, we cannot conclude that the discrepancy between the observed and calculated NO_2/NO ratio at lower altitudes provides strong evidence that expression (1) is invalid. Instead, it is apparent that the observed and calculated ratio is in better agreement than that discussed by *Evans et al.* [1976]. This is mainly a result of the larger NO abundances determined with the modified sampling and calibration procedure and to a lesser extent owing to the inclusion of better approximations for the effects of multiple scattering in the calculations of J_{NO_2}.

Comparison With Stratospheric Models

Recent reports [*National Academy of Sciences,* 1979; *Hudson,* 1979] concerning the current status of the effect of human activity on atmospheric ozone imply broad agreement between most measurements of odd-nitrogen, odd-hydrogen, and odd-chlorine and abundances calculated by atmospheric models. This broad agreement argues implicitly for the essential validity of the principal predictive working tool used in these reports—the one-dimensional stratospheric model. This type of model is meant to be representative of global average conditions but is usually run for particular conditions such as for 30°N at equinox with zonally averaged eddy-diffusion parameters. The results from a number of modeling groups have been conveniently summarized in the report by *Hudson* [1979], and it is notable that the range of concentrations for most trace species predicted by these different modeling groups is quite narrow. This likely results from the justifiable use of the same recommended photochemical and kinetic input data [e.g., *Hampson and Garvin,* 1977]. From a comparison of the then available measurements of odd-nitrogen with the range of model results, the *Hudson* [1979] report concluded that there were two significant discrepancies. First, calculated HNO_3 abundances, especially those above about 25 km, appeared much larger than most measurements. Second, upper stratospheric NO abundances were also overestimated by calculations so that both discrepancies implied an overestimate of NO_y. Reasons suggested in the *Hudson* [1979] report for the discrepancy involving NO encompassed uncertainties in estimates of eddy-diffusion parameters and in the strength of the mesospheric source of NO.

The measurements in the 18- to 21-km region by *Loewenstein et al.* [1978] indicate only a weak latitude dependence for NO from 30°–55°N in the summer and early fall. Further, the three NO profiles obtained at 32°N in fall by *Ridley and Schiff* [1980] are quite similar to the present results. Thus it is reasonable to compare the NO distribution of Figures 1–3 with the results from the 'global-average' one-dimensional models of the *Hudson* [1979] report. This is done in Figure 5. A further assessment of whether the comparison of specific experiments with these models is legitimate can be made by comparing the O_3 and temperature distributions. In Figures 4 and 5 the O_3 and temperature distributions from one of these

models (J. Chang, private communication, 1979) are compared to the 51°N measurements. Above about 30 km, the model O_3 is about twice that measured, and the model temperature is nearly 10° lower. This model calculation would therefore tend to keep more of NO_x as NO_2 above 30 km. Consequently, the observation in Figure 5 that the measured NO is about a factor of 2 larger than the model range at higher altitudes may not be significant. Certainly, the present data and that obtained at 32°N [*Ridley and Schiff,* 1981] would suggest that current models do not overestimate NO in the middle to upper stratosphere in contrast to the conclusions of the *Hudson* [1979] report. However, in the lower stratosphere, below about 23 km, the data reported here and that of *Loewenstein et al.* [1978] would indicate that these same models significantly underestimate NO. This is the altitude region where one-dimensional models are particularly sensitive to transport parameterization.

SUMMARY

A nitric oxide distribution obtained, using instrumentation with a modified air sampling and in situ calibration procedure, was found to be in good agreement with results from a previous year obtained without the instrument modification. The distributions were then combined to form an average profile which was suggested to be typical of summer conditions near 51°N. When this is compared to average measurements of NO_2 for the same latitude and season obtained by the AES, the NO_2/NO ratio is in reasonable agreement with that expected on the basis of photochemical steady state at least in the middle to upper stratosphere. At higher altitudes the range of NO measurements reported tend to be larger than but still in reasonable accord with that predicted from one-dimensional models. At lower altitudes these models estimate significantly smaller abundances of NO than are reported here.

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Correction to 'Stratospheric Odd-Nitrogen: NO Measurements at 51°N in Summer'

In the paper, 'Stratospheric Odd Nitrogen: NO Measurements at 51°N in Summer,' by B. A. Ridley and D. R. Hastie (*J. Geophys. Res. 86*, 3162, 1981) Figures 5 and 6 do not show the shading indicated by the caption. Below are the corrected figures.
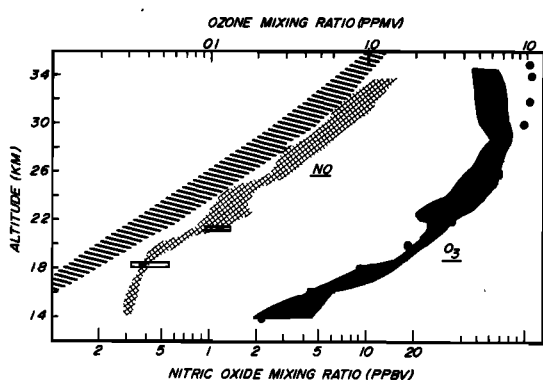

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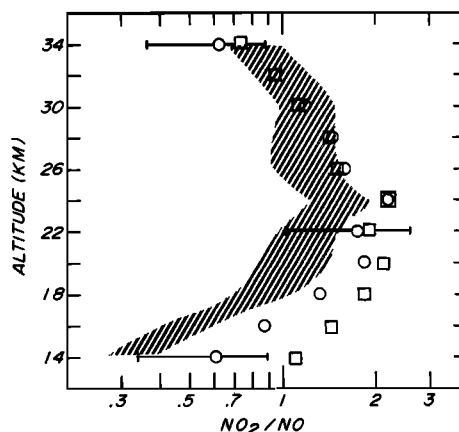
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