

Stratospheric Odd Nitrogen: Measurements of HNO₃, NO, NO₂, and O₃ Near 54°N in Winter

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Data obtained during three stratospheric measurement campaigns from Cold Lake, Alberta (100.0°W, 54.4°N), in February 1977, 1978, and 1979 are presented. Altitude profiles of NO, HNO₃, O₃, CFM-11, CFM-12, and N₂O and ground-based total column measurements of NO₂ were obtained and are compared with similar measurements made at 51°N in summer. The winter data demonstrate enhanced variability when compared with summer conditions, but in general in winter (1) there is a greater abundance of HNO₃ and the stratospheric layer is thicker, (2) there is less nitric oxide particularly in the 18- to 28-km region and the vertical distributions are characterized by strong mixing ratio gradients, and (3) the column abundance of NO₂ is lower and exhibits a diurnal change qualitatively similar to that observed in summer. The difference between the summer and winter observations is not solely due to changes in photochemistry but requires consideration of stratospheric dynamics. We correlate the reduction in NO_x in winter with the production of N₂O₅ in regions of little or no insolation followed by transport to Cold Lake. The unusual profiles are shown to result from air masses at different altitudes having either different origins, for example, polar or mid-latitude, or different transit times from the source to the sampling point.

INTRODUCTION

The observed seasonal and latitudinal behavior of odd nitrogen species in the stratosphere has recently been summarized [World Meteorological Organization, National Academy of Sciences, 1982]. A knowledge of these trends is required to assess the viability of two- and three-dimensional atmospheric models, but up until recently the success of models in reproducing some of the unusual features of experimental observations at and north of 40°N latitude has been quite limited [cf. World Meteorological Organization 1981]. Some observations that have not been well represented include the following: the dramatic summer to winter reduction of NO at 40°N for both 18- and 21-km altitudes; the order of magnitude reduction of NO north of 70° from summer to fall at 18 km [Loewenstein *et al.*, 1975, 1978a, b; Loewenstein and Savage, 1975]; the reduction in the column abundance of NO and NO₂ in winter north of 40° to 50°N [Noxon, 1979, 1980; Coffey *et al.*, 1981]; and the decrease in the column abundance of HNO₃ in spring north of 70° latitude [Murcray *et al.*, 1978].

In the 50°–60°N latitude region, wintertime observations of active odd nitrogen species would be expected to show enhanced variability when compared with summertime observations owing in part to the seasonal differences in the photolysis lifetimes of temporary reservoir species such as HNO₄ and N₂O₅. In summer the stratospheric flow is relatively weak, planetary waves are usually absent, and the average insolation is maximized and not a strong function of latitude. The abundance of active odd nitrogen in air masses from a broad geographic area may then be expected to be more uniform because the photolysis lifetimes of these reservoir species are much shorter than characteristic advection times. In contrast,

the much stronger and more variable stratospheric flow that results from the development of planetary waves in winter may strongly couple the dark polar region, or at least regions of low average insolation, to the observation site at 50°–60°N. Photolysis lifetimes of reservoir species may be longer or comparable to advection times from more northerly source regions. Thus the abundance of related and photochemically active species like NO_x and, for example, N₂O₅ at a particular location is expected to depend strongly upon the residence time of the air mass in the polar region and upon the insolation experienced during transit to the observation site. Such considerations led Knight *et al.* [1982] to conclude that N₂O₅ was likely a significant reservoir of NO_x in winter at high latitudes. Solomon and Garcia [1983a] have since shown that their two-dimensional model predicted, after HNO₃, N₂O₅ to be the second most abundant odd nitrogen species below 28 km in the northern winter stratosphere.

Our interest in the northern winter stratosphere was generated by a series of papers by Noxon and co-workers [Noxon *et al.*, 1979a, b, 1983; Noxon, 1979, 1980], who observed that the stratospheric column abundance of NO₂ exhibits marked temporal, seasonal, and latitudinal variations, especially north of 40°N latitude. One of the most interesting wintertime observations was a very sharp reduction in the column abundance of NO₂ between 45 and 50°N, now often referred to as the Noxon "cliff." For example, in February 1977, the evening twilight abundance decreased from $6.3 \times 10^{15} \text{ cm}^{-2}$ at 45°N to $1.6 \times 10^{15} \text{ cm}^{-2}$ at 50°N. In addition, Noxon [1979, 1980] found that south of the cliff there was a marked difference between the morning and evening NO₂ column abundance, while north of the cliff the diurnal change was virtually absent. Later work has shown that the latitudinal cliff was not a permanent feature of the winter stratosphere but was dependent upon the boundary of the low-pressure vortex flow traversing western North America in the 40°–45°N region.

Noxon and co-workers have also shown that the NO₂ column abundance at higher latitudes in winter at a particular

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TABLE 1. Flight Information

Date	Launch Time, LT*	Start		Float Period Altitude, km	Termination	
		Time, LT	Position		Time, LT	Position
Feb. 19, 1977	0750	1000	53.0°N, 109.0°W	29.3	1700	51.1°N, 106.5°W
Feb. 14, 1978	0955	1200	54.0°N, 110.7°W	31.3	1515	52.6°N, 111.5°W
Feb. 11, 1979	1306	1545	54.2°N, 109.0°W	33.0	2000	53.6°N, 109.2°W

*UT = LT - 7 hours.

observation site was very sensitive to the air mass trajectory. For example, the column abundance remained low within the portion of the polar vortex that split and moved rapidly over southwestern Canada during the stratospheric warming of late February 1979.

At the time of the *World Meteorological Organization* [1981] report, attempts at modeling even a stable dynamic situation for winter conditions failed to yield the cliff feature. More recently, *Solomon and Garcia* [1983a, b] have made considerable progress in synthesizing a cliff by using their two-dimensional model combined with particular air mass trajectories. They have demonstrated in detail the strong interactions of wintertime photochemistry and dynamics.

In this work we attempted to obtain information about the seasonal changes in the altitude distribution of some of the odd nitrogen species at northern latitudes over a three-winter measurement program. We begin with a brief description of the measurement techniques, present the observations, and compare them with our summer observations and with the results from other groups. The data are first discussed only in terms of expected changes from summer to winter due to photochemistry. In the final section we show that stratospheric dynamics must also be considered to explain some of the observations. Throughout this paper, NO_x is defined as the sum of NO and NO_2 , while NO_y is reserved for the sum of all the odd nitrogen species, i.e., $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HNO}_4 + \text{HNO}_2 + \text{ClONO}_2 + \text{N}$.

OBSERVATIONS AND COMPARISONS WITH OTHER DATA

The balloon payloads were launched from Canadian Forces Base, Cold Lake, Alberta (110.0°W, 54.4°N), during February of 1977, 1978, and 1979. Altitude profiles of O_3 , HNO_3 , NO and temperature were determined from each flight. In 1977 only, grab samples were collected on parachute descent and analyzed in the laboratory to determine the N_2O , CF_2Cl_2 (CFM-12) and CFCl_3 (CFM-11) content. Ground-based measurements of the stratospheric column abundance of NO_2 were also made during each field trip.

The flights in 1977 and 1978 were conducted under normal winter stratospheric vertical temperature distributions. The flight in 1979 occurred during a stratospheric warming. Some results from this latter flight have been reported previously [Knight *et al.*, 1982; Evans *et al.*, 1982]. Table 1 summarizes the measurement times and indicates the approximate trajectory for each flight.

A data base for summer conditions near this latitude is required for comparison with the winter observations. We have used the results of a number of summertime measurements from Yorkton, Saskatchewan (102°W, 51.3°N), and Gimli, Manitoba (97.1°W, 50.6°N), using essentially the same instrumentation, to provide this base. The choice for the summer altitude profiles is as follows: NO, O_3 and temperature are averages taken from *Ridley and Hastie* [1981]. The

NO_2 distribution for high sun conditions is estimated by averaging the morning and evening average NO_2 profiles of *Kerr et al.* [1982]. The choice of a representative distribution of HNO_3 is more difficult. The altitude of the peak mixing ratio in HNO_3 in summer varies from flight to flight so that the average profile of *Evans et al.* [1978] broadens the distribution and reduces the observed peak mixing ratio. Consequently, we present both the average summer distribution and a single profile from a flight from Yorkton in August 1976.

Nitric Acid

Altitude profiles of HNO_3 were derived from measurements of the thermal emission in the 11.3- μm band made with a liquid nitrogen cooled scanning radiometer. The instrument was similar to the fixed wavelength filter radiometer described by *Evans et al.* [1976]. The absolute response of the instrument was determined at the launch site by calibration against a variable but temperature-controlled cold target of known emissivity. Details of the data reduction method have been described previously [Evans *et al.*, 1976].

Figures 1, 2, and 3 show the mixing ratio of HNO_3 determined from each winter flight along with the summer profiles discussed previously. The winter 1978 and 1979 profiles are similar overall with marginally more HNO_3 in the 20- to 24-km region and less above 29 km in 1979. This repeatability

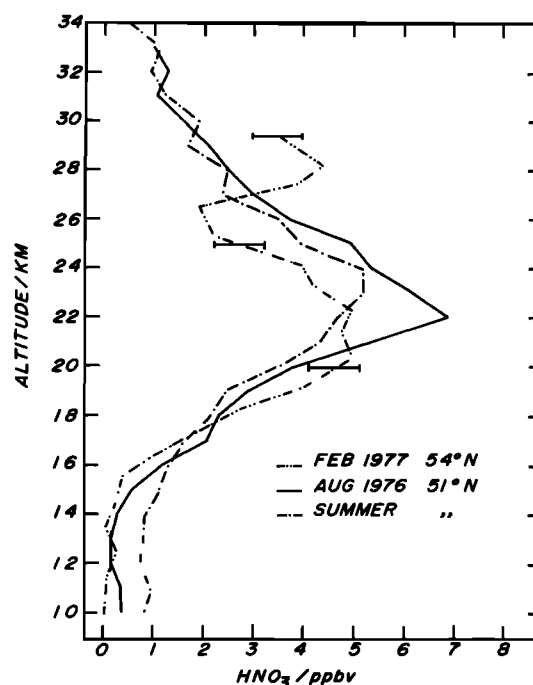


Fig. 1. Nitric acid distributions for February 19, 1977, August 28, 1976 [Evans *et al.*, 1981], and a summer average for 51°N [Evans *et al.*, 1978]. The error bars indicate the expected random errors which are in addition to the 15% uncertainty in the radiance data.

would not be expected in view of the long photolysis lifetime of HNO_3 especially at low altitudes (~ 12 days at 30 km, ~ 100 days at 20 km). The distributions should be controlled principally by stratospheric dynamics. In contrast, the 1977 winter profile appears more like the summer distribution below 25 km with a layer of enhanced mixing ratio beginning at 26 km.

There is no clear evidence as to which profile is more typical of the winter stratosphere, but a comparison with measurements made from aircraft flights suggests that the 1978 and 1979 profiles are more usual. Coffey *et al.* [1981] have reported a strong latitudinal increase in the wintertime column abundances above 12 km with 50°N values ranging from 8.5 to $12 \times 10^{15} \text{ cm}^{-2}$ for February 1978 and December 1979 to February 1980. There also appears to be a much greater variation in the winter column abundances than for summer. Similarly, Murcray *et al.* found values of 8 and $12 \times 10^{15} \text{ cm}^{-2}$ at 40° and 60°N , respectively, in January 1974 [Murcray *et al.*, 1975] and 6.5 , 15.5 , and $15 \times 10^{15} \text{ cm}^{-2}$ at 35° , 54° , and 60°N , respectively, in the spring of 1975 [Murcray *et al.*, 1978]. More recently, Gille *et al.* [1984] have deduced a seasonal change at northern latitudes from satellite observations. At 55°N the May and November abundances were 10 and $17 \times 10^{15} \text{ cm}^{-2}$, respectively.

The column abundances determined from the balloon profiles are 6.8 , 10.6 , and $12.6 \times 10^{15} \text{ cm}^{-2}$ for February 1977, 1978, and 1979, respectively, so that the latter two profiles appear to be more typical of the northern winter stratosphere. Figures 2 and 3 show that the additional wintertime nitric acid appears both above 25 km and below 19 km. Since the photochemical production of HNO_3 by reaction of OH with NO_2 is greatly reduced at high latitudes owing to very low average insolation, the thickening of the layer may be due to poleward and downward transport of this long-lived species. A similar pattern occurs for O_3 .

With the exception of the upper layer above 26 km the 1977 winter profile more nearly resembles the average summer profile. The column abundance of $6.8 \times 10^{15} \text{ cm}^{-2}$ is, however, significantly less than the $9.7 \times 10^{15} \text{ cm}^{-2}$ of the average

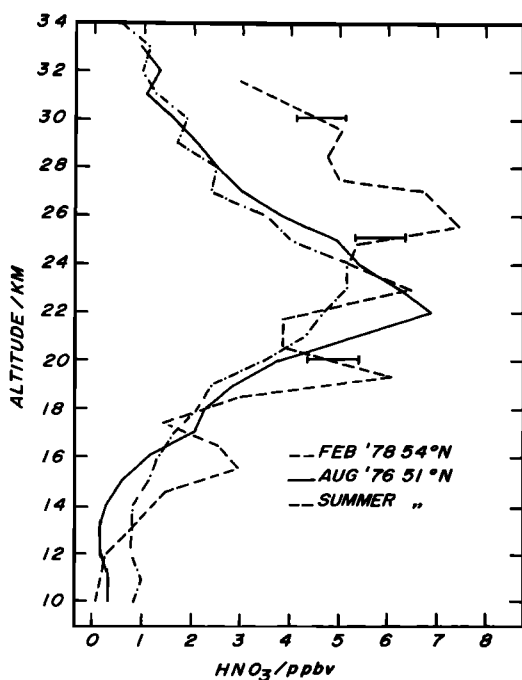


Fig. 2. As in Figure 1 for the February 14, 1978, winter flight.

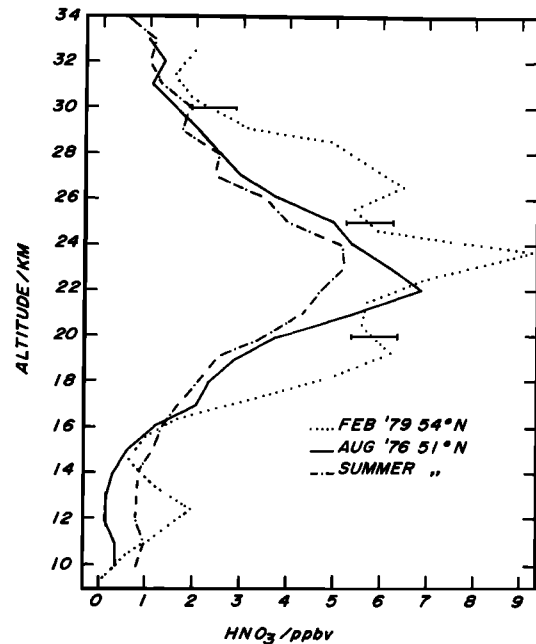


Fig. 3. As in Figure 1 for the February 11, 1979, winter flight.

summer profile or the $9.0 \times 10^{15} \text{ cm}^{-2}$ of the Yorkton profile. On the basis of the strong latitudinal dependence of HNO_3 observed in the aircraft measurements discussed above, the low column abundance would imply that the source of the air mass sampled below 26 km in 1977 was recently from mid-latitudes.

Nitric Oxide

In situ measurements of NO were made during balloon ascent and at float with a chemiluminescence instrument modeled after that described by Ridley and Howlett [1974]. The instrument used in 1978 and 1979 incorporated the air sampling and on-board calibration modification described by Ridley and Schiff [1981], whereas the instrument used in 1977 did not. It is possible that the measured mixing ratios in 1977 could have been lower than the ambient values owing to losses of NO on the walls of the air sampling tube upstream of the point of addition of the on-board calibration gas. In retrospect it is impossible to assess the magnitude of any such losses. As there are some definite similarities in both the shapes of all three winter profiles and in the magnitude of the observed mixing ratios, it appears that wall losses during the 1977 flight were small. However, the results of calculations that employ the 1977 data must be regarded as less conclusive than those based on succeeding flights.

The data are shown in Figures 4, 5, and 6. The average summer profile for 51°N is included in each figure to illustrate the seasonal differences. Figure 7 shows that a small increase in NO occurred during the 3-hour float period of the 1977 flight. This increase is likely due to the photolysis of an odd nitrogen reservoir species to yield active NO_x ; a plausible candidate is N_2O_5 . Float data from the 1979 flight that mapped the sunset decay of NO may be found in the work of Knight *et al.* [1982]. Each of the profiles, but especially those of 1977 and 1978, exhibited a region of a remarkably strong increase in the mixing ratio with altitude. The onset of this rapid increase was at a different altitude each year. In 1977 and 1978 it occurred near 27 and 23 km, respectively, while in 1979 there were two weaker gradient regions, one started near 22 km and the other near 28 km. Such a strong layering of the

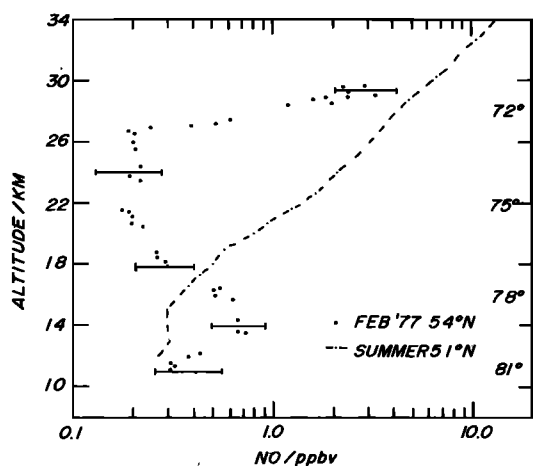


Fig. 4. The NO distribution for February 19, 1977, compared with an average summer profile for 51°N from Ridley and Hastie [1981].

mixing ratio of NO would be almost impossible to achieve by photochemistry and simple diffusion. Therefore the strong layering must have been due to transport processes. Below the upper layer of NO, each profile also exhibited a region where the mixing was much lower than was observed in summer. In 1979 this region of low mixing ratio extended to the lowest altitudes at which measurements were made, almost to the tropopause. The 1978 data behaved similarly overall, but there was also considerable structure below 20 km with some sharp maxima approaching or exceeding the summer average. In contrast the 1977 profile exhibited low values between 18 and 26 km, an upper layer above 26 km, and a lower layer centered near 14 km.

The predominant difference between the winter and summer distributions of NO at 51°–54°N latitude was the greatly reduced NO in the lower to mid stratosphere in winter. At the highest altitudes sampled, 30–32 km, the winter and summer mixing ratios were not very different. At the lowest altitudes sampled, 12–18 km, the winter abundance was highly variable and on two of three occasions lower than in summer. The greatest reduction occurred in winter roughly in the 18- to 28-km region. There was, however, much greater variability among the three winter profiles than was observed in summer.

Loewenstein and Savage [1975] and Loewenstein et al. [1978a, b] observed little variation in the NO concentration at

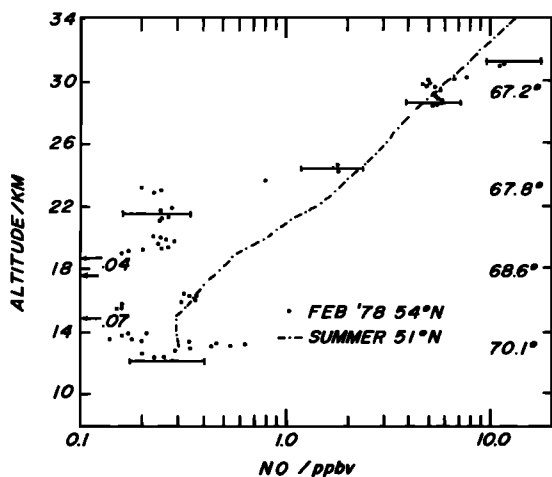


Fig. 5. As in Figure 4 for February 14, 1978.

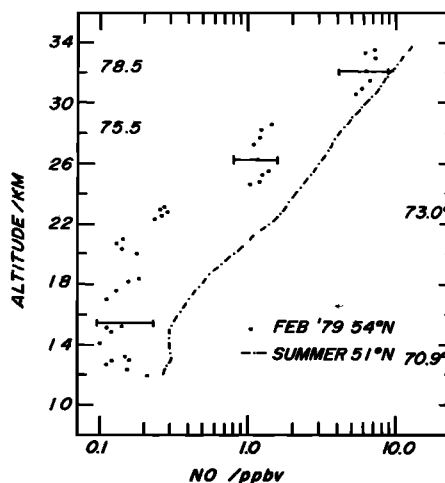


Fig. 6. As in Figure 4 for February 11, 1979.

55°N between spring, summer, and autumn at either 18 or 21 km. North of 65° the mixing ratio observed in autumn was substantially lower. For example, in the 70°–80°N region, the NO mixing ratio was 0.1 ppbv in autumn and 0.5 ppbv in summer at 18 km, and it was 0.5 ppbv in autumn and 1.5 ppbv in summer at 21 km.

Loewenstein et al. [1975] have also reported a marked seasonal variation of NO at both 18 and 21 km from a number of aircraft missions at 40°N. Minimum values at 21 km of 0.1 to 0.3 ppbv were observed in December and January and 0.1 to 0.5 ppbv in February. In summer there was a broad maximum with values in the range of 0.5 to 1.2 ppbv. I. E. Galbally et al. (unpublished manuscript, 1983) have reported a profile of NO in autumn at 34°S that resembles our winter profiles. They attributed the reduction in NO at low altitudes to a combination of south to north transport and a shift in the photochemical partitioning between NO_x and HNO₃.

Coffey et al. [1981] have reported measurements of the column abundance of NO above 12 km from near the equator to about 50°N in summer and winter. Little seasonal change was observed until north of 40°. At 50°N a late afternoon winter column abundance of about $1.7 \times 10^{15} \text{ cm}^{-2}$ was reported. On February 14, 1978, the afternoon column abundance near 50°N was $\sim 2.3 \times 10^{15} \text{ cm}^{-2}$, and the morning abundance was a factor of 2.5 lower. The column amounts from our balloon measurements are about 2.9, 3.6, 2.0, and $5 \times 10^{15} \text{ cm}^{-2}$ for 1977, 1978, 1979, and summer, respectively. These are larger than the aircraft measurements but are well within the uncertainty of the two methods. There is clearly a decrease in both the column amount of NO and in the mid stratosphere mixing ratio at these latitudes in the winter.

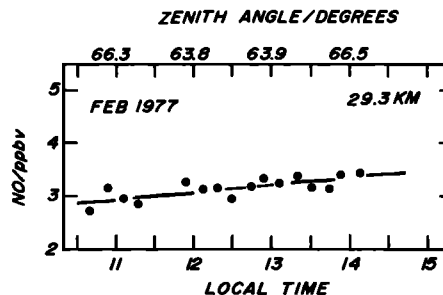


Fig. 7. The growth of NO at 29.3 km during the February 19, 1977, flight.

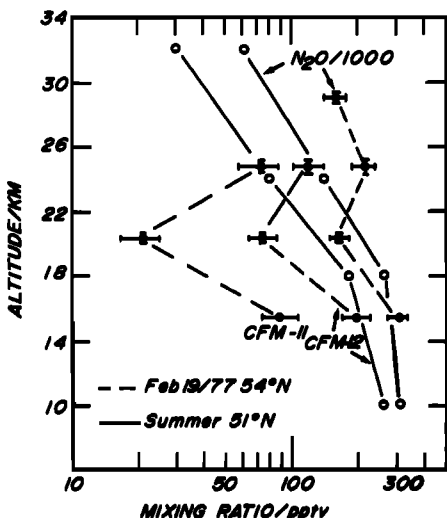


Fig. 8. N₂O and fluorocarbon results obtained during the February 19, 1977, flight compared with data obtained in August 1977 at 51°N.

Nitrous Oxide and Chlorofluoromethanes (CFM)

In 1977, whole air samples were collected on parachute descent using sample containers obtained from and prepared similarly to the method developed by the National Oceanic and Atmospheric Administration Aeronomy Laboratory [Schmeltekopf et al., 1976]. As it was not possible to have an isolated parachute descent and recovery of the grab sample system, the sampling spheres were positioned in the gondola such that all the air sample inlet tubes projected into an aluminum skirt that extended well below the bottom of the gondola to minimize contamination by the payload. One sphere was crushed on surface impact, but the remaining samples were analyzed in the laboratory using an electron capture gas chromatograph.

The results, along with those from a summer flight from Yorkton in August 1977, are shown in Figure 8. The winter profiles show a folded distribution that is quite dramatic but not unlike one observed for N₂O in Alaska in May 1976 by Schmeltekopf et al. [1977]. Less strongly folded distributions have been frequently observed by other groups.

In the 15- to 20-km region the decrease in mixing ratio with

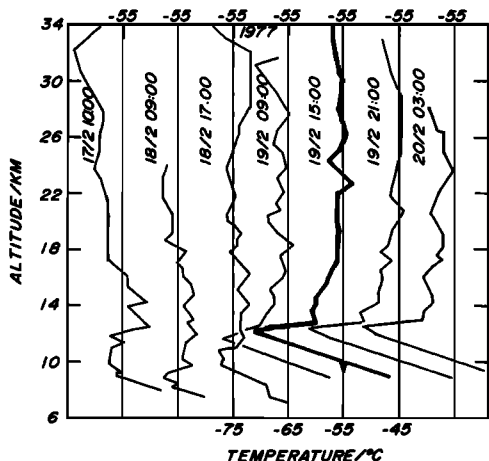


Fig. 9. Temperature profiles obtained from ozone sonde releases during February 1977. The profiles are shifted by 10° for clarity. The lower temperature scale belongs to the heavier profile marked with an arrow.

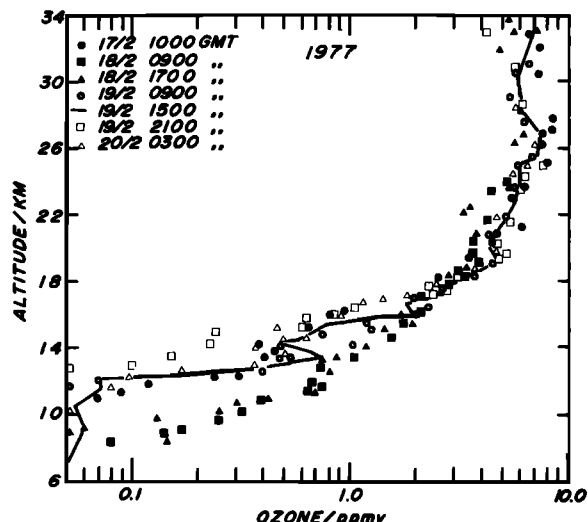


Fig. 10. Ozone mixing ratio profiles for February 1977.

altitude for CFM-12 and N₂O is similar for the two seasons. If the data are referenced to the altitude above the average tropopause [cf. Goldan et al., 1980], the data coincide. Above 22 km the winter profiles show a layer of enhanced abundance, and although we cannot resolve the sharpness of the layer, the start of the enhancement was only a few kilometers below the onset of the increase in NO and HNO₃. Thus all the profiles of 1977 (NO, HNO₃, CFM-11, CFM-12, and N₂O) show an increase in mixing ratio at higher altitudes (~25 km) that points to a variation in the source of the air mass with increasing altitude.

Ozone Sonde Observations

A number of electrochemical cell sondes were flown during the period of each campaign from the meteorological station at Primrose Lake located about 50 km north of CFB, Cold Lake. These served two functions: to provide O₃, temperature, and wind vectors coincident with the odd nitrogen observations and to provide temporal information concerning the stability of the stratosphere prior to the launch of the main payload.

1977. The temperature, O₃, and wind component profiles are shown in Figures 9, 10, and 11. It is convenient to discuss the observations in the altitude regions above and below about 18 km.

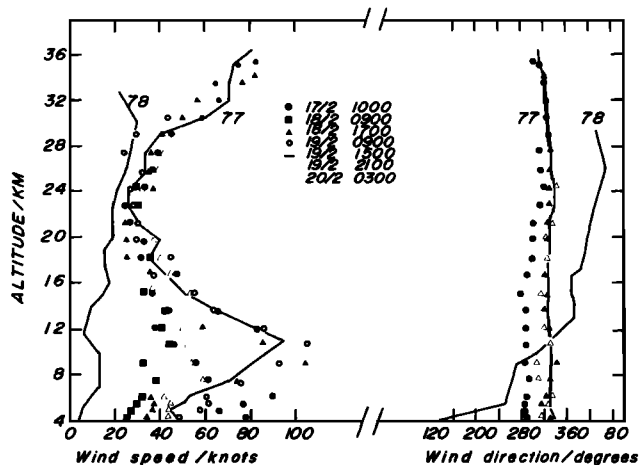


Fig. 11. Wind speed and direction from some ozone sonde releases during February 1977 and 1978.

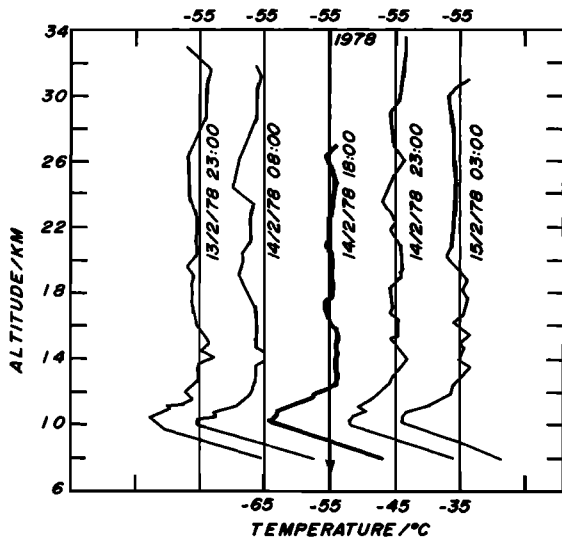


Fig. 12. As in Figure 9 for February 1978.

Above 18 km there are only minor differences in all three parameters during the observation period. There are some small variations in the O_3 profiles, but the differences above about 28 km probably reflect the decreasing accuracy of the measurement technique rather than actual variability. An increase of air temperature occurred between February 17 and 18, but the succeeding profiles show an isothermal atmosphere of -55°C above 18 km. The wind speed was relatively constant and its direction shifted slightly to more northerly flow during the observation period. Thus in this altitude region above the Cold Lake vicinity, the atmosphere appeared quite stable for several days prior to the odd nitrogen measurements. There was no obvious change in any of these local observations that would suggest a dynamic cause for either the upper layer in HNO_3 , the strong NO gradient, or the folded CFM and N_2O profiles.

In contrast, below 18 km, substantial changes in wind speed, O_3 , and air temperature were evident. Starting late on February 18, the tropopause height, as defined by the change in temperature lapse rate, was driven upward by nearly 3 km by the northward meander of the jet stream, leaving Cold Lake south of the jet core. Also, on February 17, the altitude

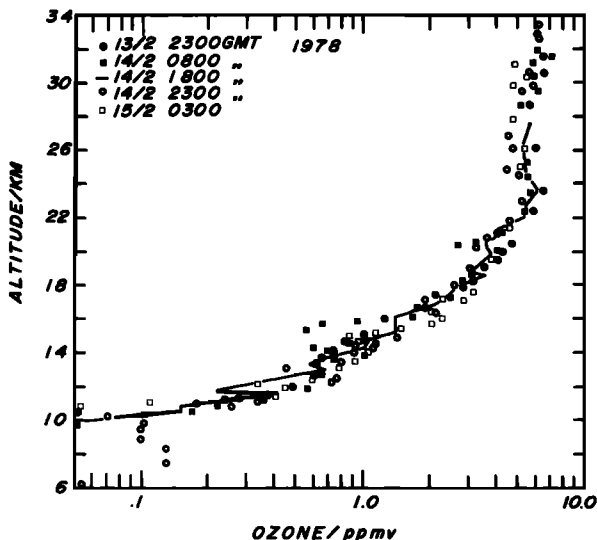


Fig. 13. Ozone mixing ratio profiles for February 1978.

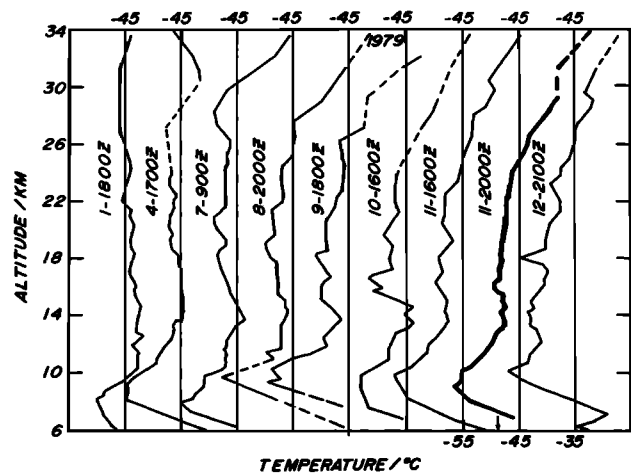


Fig. 14. As in Figure 9 for February 1979.

at which the temperature lapse rate changed was lower than that corresponding to the rapid increase in O_3 mixing ratio. This suggests that some tropospheric/stratospheric exchange may have occurred at low altitudes prior to the balloon flight. In fact, the peak in the NO mixing ratio at low altitudes would be consistent with the intrusion of tropospheric air on the equator side of the jet if the upper troposphere were rich in NO. Intuitively, though, one would expect the upper troposphere to be poor in NO_x relative to the stratosphere. Thus an alternate explanation of the low-altitude peak must be sought.

1978. Although the observation period in 1978 was quite short, it is evident from Figures 11, 12, and 13 that the stratosphere above Cold Lake did not undergo significant changes for at least a day and a half prior to the odd nitrogen flight. The wind speed and direction data were so similar that only the data from the sonde closest in time to the large balloon flight is given. Compared with 1977, the wind speeds were much lighter at all altitudes. Again there are no meteorological data which would simply explain the strong NO mixing ratio gradient near 23 km.

1979. There was a moderate stratospheric warming peak on January 26 and another on February 7 [Quiroz, 1979]. The substantial changes in wind components and air temperature, shown in Figures 14 and 16, reflected this instability. There were also substantial changes in the wind components over

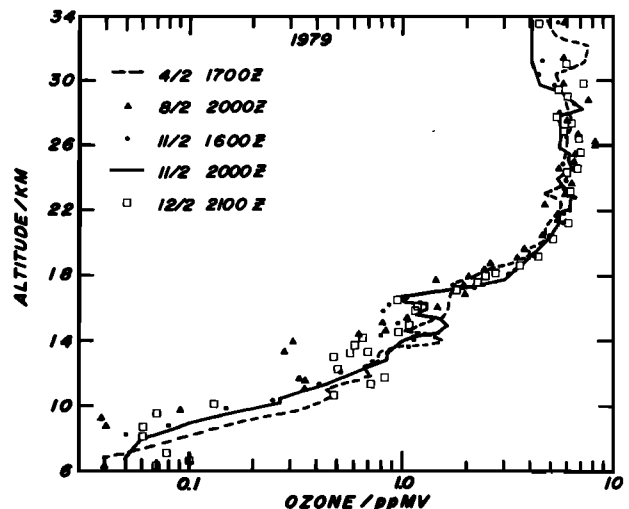


Fig. 15. Ozone mixing ratio profiles for February 1979.

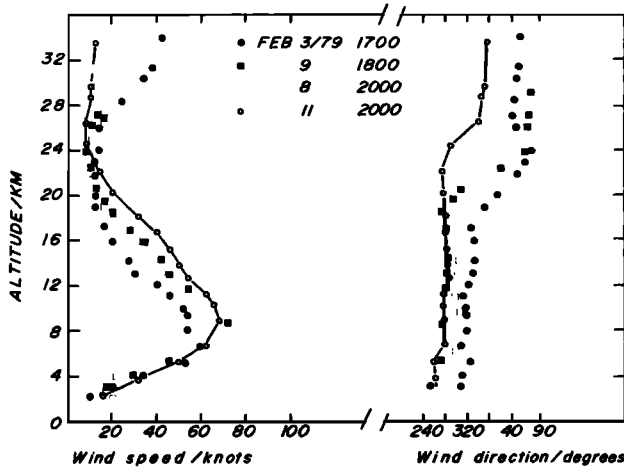


Fig. 16. Wind speed and direction from some ozone sonde releases during February 1979.

Cold Lake especially above 20 km. Wind speeds were very light by the time of the balloon flight, but a gradual shift to more northerly flow also occurred. The atmosphere was nearly isothermal at -45°C , 10° warmer than in 1977 or 1978, at the first of the month. But between February 4 and 12 a downward propagation of increasing temperatures and a slight cooling in the 12- to 22-km region occurred. Again the unstable tropopause height reflected the movement of the jet stream south of Cold Lake.

Figure 15 shows that, as in 1977, there were substantial changes in the daily O_3 mixing ratio between 12 and 18 km. Between 18 and 28 km the O_3 mixing ratios were remarkably constant.

Ground-Based NO_2 Observations

The stratospheric column abundance of NO_2 was measured using the twilight absorption method first developed by Brewer *et al.* [1973, 1974] and later modified for this work. The instrument employed a modified 15-cm Ebert spectrometer, having 0.4-nm resolution, set to monitor the zenith sky intensity at five wavelengths, 437.8, 439.3, 442.0, 444.9, and 450.1 nm corresponding to alternate maxima and minima in the highly structured NO_2 absorption spectrum. The NO_2 and ozone absorption coefficients at these wavelengths are given in Table 2 and are values obtained from H. S. Johnston (private communication, 1982). From observations of the variation of the zenith sky intensity as a function of the solar zenith angle near twilight the stratospheric column abundance can be determined. The deconvolution procedure minimizes possible interference by ozone and water vapor and is similar to that described by Kerr *et al.* [1982]. Some details of the procedure used for ground-based observations have been de-

TABLE 2. Absorption Coefficients at the Five AES NO_2 Wavelengths

Wavelength λ , nm	NO_2 Absorption Coefficient α , cm^{-1}	O_3 Absorption Coefficient α , cm^{-1}	Rayleigh Scattering Coefficient, atm^{-1}
437.8	4.979	9.5×10^{-4}	0.1086
439.3	8.134	11.8×10^{-4}	0.1071
442.0	4.457	18.0×10^{-4}	0.1045
444.9	7.728	18.4×10^{-4}	0.1019
450.1	4.871	19.8×10^{-4}	0.0972

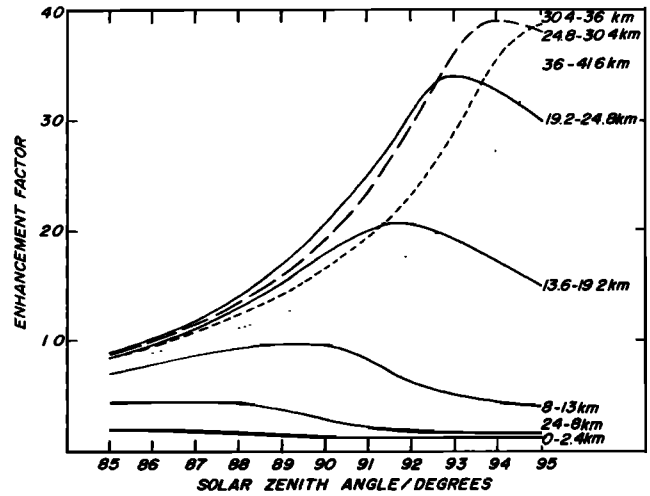


Fig. 17. Model results of the absorption enhancement factor as a function of the solar zenith angle and the height of the absorbing layer of NO_2 .

scribed by Brewer *et al.* [1974] and by Syed and Harrison [1980]. Further details of the method follow.

A layer of NO_2 in the atmosphere reduces the intensity of light scattered from the zenith sky to the ground for wavelengths between 400 and 500 nm where the NO_2 absorption coefficient is appreciable. The degree to which the light is attenuated is a function of the height of the absorbing layer and the solar zenith angle of the sun. For a layer of NO_2 near the surface, as is typical of most pollution situations, the path length through the attenuating layer is vertical because the source of the scattered light is well above this layer. For a layer at the top of a plane atmosphere, the path length is enhanced in relation to the vertical by a factor equal to the secant of the solar zenith angle because most of the light passes through the layer with the direct solar beam before being scattered toward the surface. Since in the real world the atmosphere is spherical and NO_2 is distributed vertically between the ground and the top of the atmosphere, the absorption enhancement factor varies between 1 and the secant of the solar zenith angle. For a layer of NO_2 in the stratosphere, above about 15 km, the enhancement factor is quite large for zenith angles between 85° and 95° enabling a twilight measurement of stratospheric NO_2 .

In order to determine the enhancement factor as a function of layer height and solar zenith angle, a multiple scattering radiative transfer computer model was used. The model was originally developed by Dave [1964] and later applied to ozone Umkehr analysis [DeLuisi and Mateer, 1971]. Results of the model calculations for the enhancement factors of NO_2 absorption are shown in Figure 17. The intensity of light arriving at the ground of wavelength n (i.e., λ_n , $n = 1$ to 5) is given by

$$\log I_n = \log I_{on} - \alpha_n Y - \alpha_n' Z - \beta_n m \quad (1)$$

where

- I_n the measured light intensity outside the atmosphere at λ_n ;
- I_{on} the light intensity outside the atmosphere at λ_n ;
- α_n the NO_2 absorption coefficient at λ_n , cm^{-1} ;
- Y the effective path length of NO_2 , cm;
- α_n' the O_3 absorption coefficient at λ_n , cm^{-1} ;
- Z the effective path length of O_3 , cm;
- β the Rayleigh scattering coefficient at λ_n , atm^{-1} ;
- m the effective air mass, atm.

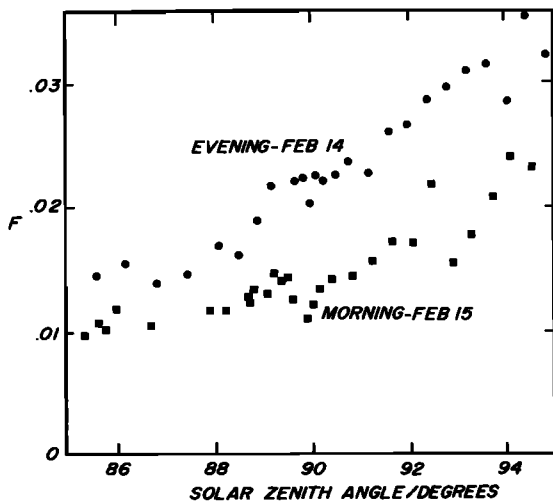


Fig. 18. Sample zenith sky absorption measurements made from Cold Lake in February 1977.

The light intensities at the five wavelengths given in (1) are combined linearly to form the following expression:

$$F = F_0 - \sum \alpha Y - \sum \beta m \quad (2)$$

where

$$F = \log I_1 - 1.28 \log I_2 + 0.97 \log I_3 - 1.29 \log I_4 + 0.61 \log I_5$$

$$F_0 = \log I_{01} - 1.28 \log I_{02} + 0.97 \log I_{03} - 1.29 \log I_{04} + 0.61 \log I_{05}$$

$$\sum \alpha = \alpha_1 - 1.28\alpha_2 + 0.97\alpha_3 - 1.29\alpha_4 + 0.6\alpha_5 = 8.16 \text{ cm}^{-1}$$

$$\sum \alpha' = \alpha'_1 - 1.28\alpha'_2 + 0.97\alpha'_3 - 1.29\alpha'_4 + 0.6\alpha'_5 \sim 0$$

$$\sum \beta = \beta_1 - 1.28\beta_2 + 0.97\beta_3 - 1.29\beta_4 + 0.6\beta_5 \sim 0$$

If the values from Table 2 are substituted into the $\sum \alpha$, $\sum \alpha'$, and $\sum \beta$ expressions, the values shown above are derived. The expression F in (2) above is therefore linearly proportional to the amount of NO_2 in the effective path and is insensitive to ozone.

Figure 18 shows sample twilight observations for the evening of February 14 and the morning of February 15, 1977. The amount of stratospheric NO_2 is determined by comparing the measured absorption curves in Figure 18 with the computed enhancement factor curves in Figure 17. The observed curves are fitted to each of the five model curves above 13.6 km, and residual errors are determined for the NO_2 layers at

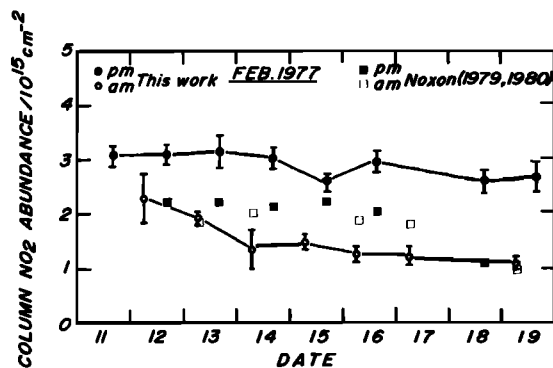


Fig. 19. Evening and morning twilight column abundances of stratospheric NO_2 . The data points on February 15 were obtained at Primrose Lake. Noxon's data [Noxon, 1979] for February 18 and 19 were obtained at 50.3°N.

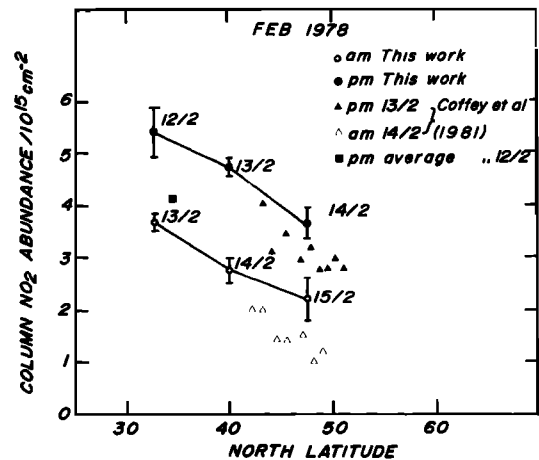


Fig. 20. NO_2 column abundances during February 1978.

each of the five altitudes. The amount of NO_2 assigned to each layer is then made proportional to the inverse of the residual error at the corresponding layer, thereby establishing an approximate vertical profile. It was found that residual errors were usually reduced by about 20% when the five-layer procedure was employed as opposed to one in which all of the NO_2 was assigned to a single stratospheric layer. This latter procedure is essentially that used by Noxon *et al.* [1979a].

There are a number of error sources for a twilight zenith sky NO_2 measurement. The method is inherently insensitive to the presence of NO_2 in the lowest altitude region of the stratosphere (cf. Figure 17). Changes in the NO_2 abundance between the wintertime tropopause and about 15 km cannot be accurately resolved. The inversion technique also assumes spatial and temporal homogeneity. Rapid day-to-day NO_2 variations, such as those which are observed in stratospheric warming situations, suggest that significant horizontal gradients may occur. Also the conversion of NO_2 to NO at sunrise and NO to NO_2 at sunset could cause a systematic bias of the measurements. Because of evening twilight NO to NO_2 conversion, the method yields a value for the NO_2 column amount which is calculated to be 10–20% larger than the daytime amount. Another error source is the effect of low-level pollution on the measurements. Even though the enhancement factors are relatively small for NO_2 near the ground (Figure 17), the amount of NO_2 that is present near urban centers can cause significant absorption on a zenith sky measurement. In a static situation this problem is not too serious because the main effect of low-level pollution is to increase uniformly the twilight absorption curve for solar zenith angles between 85°

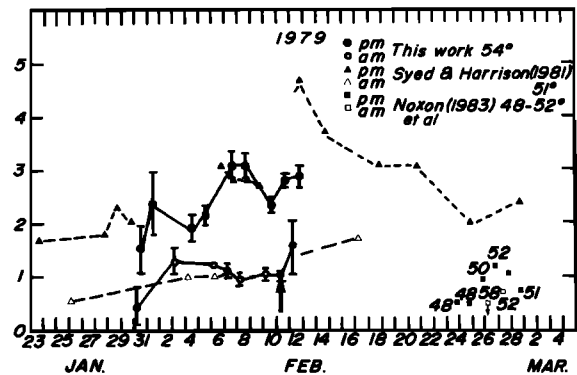


Fig. 21. NO_2 column abundances during February 1979. The abscissa scale is in units of 10^{15} cm^{-2} .

and 95°. The analysis of stratospheric NO₂ depends mainly on the shape of the twilight absorption curve, and a vertical uniform displacement of the curve has very little effect on the final NO₂ column amount. In fact, a low-level pollution variable is included in the least squares curve-fitting analysis, and a pollution parameter is determined. The main problem arising from the presence of pollution is the variations of ground level NO₂ during the change in zenith angle. These variations can distort the shape of the absorption curve and cause significant errors ($\pm 20\%$) in the stratospheric NO₂ estimate.

The error for an individual twilight measurement is estimated by using the residual error derived from the fit of the model distribution to the observed curve. Error bars indicated in Figures 19, 20, and 21 were derived in this manner.

In 1977, observations were made from either the launch site or from Primrose Lake. Also during this period, Noxon [1979, 1980] completed a latitude survey from Boulder, Colorado, to Cold Lake. In 1978 a latitude survey of column NO₂, using the AES spectrometer, was scheduled to finish at Cold Lake just prior to the balloon launch. Unfortunately, the instrument was damaged beyond field repair during shipment on a commercial flight into Calgary. In 1979, measurements were made just at the launch site.

The results for 1977 are given in Figure 19. In contrast to the limited data base for NO and HNO₃ at this latitude in winter there exists an abundance of NO₂ column data [Noxon, 1979, 1980; Noxon *et al.*, 1979b, 1983; Syed and Harrison, 1981a, b; Coffey *et al.*, 1981]. Where these measurements coincide in time, their results are included in the figures. However, it is important to realize that all of these data may underestimate the true winter vertical column abundance because the twilight method is not very sensitive to NO₂ at low altitudes in the stratosphere. Noxon *et al.* [1979a] report that their method is insensitive to NO₂ below about 15 km, the AES technique is limited to altitudes above 13–14 km, and the aircraft measurements were made for altitudes above 12 km. With a normal winter tropopause near 9 km, and for a conservatively low NO₂ mixing ratio between 9 and 15 km of 100–200 pptv, a column contribution of 0.4 to 0.8×10^{15} cm⁻² would be missed in the ground-based methods. This is a significant fraction of the lowest winter column abundances shown in Figures 19 and 21. In summer the amount missed would likely be a much smaller fraction of the values reported, owing to the larger abundance and higher tropopause. Consequently, the seasonal change reported for this latitude [Syed and Harrison, 1981b; Noxon, 1979, 1980] may be somewhat overestimated.

The evening column abundances of Figure 19, determined with the AES spectrometer in 1977, are fairly constant. The average is $2.9 \pm 0.2 \times 10^{15}$ cm⁻² (excluding the measurement at Primrose Lake). In contrast the morning abundances show a systematic decline from February 12 to 14 and remain constant thereafter.

Included in Figure 19 are the measurements made at Cold Lake and at Primrose Lake in 1977 by Noxon [1979, 1980]. He departed from Cold Lake on February 18 so that the points for February 18 and 19 were actually obtained at 50.3°N. There are two differences in the data sets. First, Noxon's corrected evening abundances are on average about 30% lower than the values obtained using the AES spectrometer. Syed and Harrison [1980] have pointed out that the differences in the Noxon and AES method of determining twilight enhancement factors would lead to such a difference.

A more important concern is the difference between the morning and evening twilight column amounts. Noxon [1979, 1980] observed essentially no diurnal variation, a result which he interpreted as being characteristic of conditions north of the NO₂ cliff. In contrast, the average P.M. to A.M. ratio determined here is 1.8. This discrepancy is still inexplicable. Unfortunately, the importance of N₂O₅ as a northern winter reservoir of odd nitrogen is linked indirectly to the existence or nonexistence of a diurnal variation in NO₂.

The results from the interrupted latitude survey of 1978, shown in Figure 20, indicate a gradual decline in evening and morning column abundance up to 47°N during the time prior to the balloon flight. It would appear that more northerly observations could have extrapolated to values at least as low as those observed in 1977 at 54°N, but there is no guarantee of this, in view of the sensitivity of column NO₂ to changes in stratospheric flow [Noxon, 1979; Noxon *et al.*, 1979b, 1983]. Included in the figure are the morning and evening abundances above 12 km determined from solar absorption spectra by Coffey *et al.* [1981]. Although the data at 34°N are notably disparate, the data northward of 40° are within the combined uncertainty of each set of measurements. It is unfortunate that neither data set extends to 54°N because the stratospheric flow in this region in 1978 was quite different from that in 1977. No correlation between column abundance and flow can be attempted. Nevertheless, we are confident a diurnal change in the column abundance should have occurred above Cold Lake, since Coffey *et al.* observed an evening to morning ratio of NO₂ at 51°N of 2.8. Their ratio is, however, larger than observed by us at 48°N in 1978 or at Cold Lake in 1977.

The results for 1979 are shown in Figure 21 [Evans *et al.*, 1982]. Both the evening and morning column amounts are more variable in comparison with the 1977 data. Prior to the moderate warming peak of February 7, the evening abundance was about 30% lower than observed in 1977 but increased after that date to an almost identical value. Again, a diurnal variation is deduced from the observations. Prior to February 7 the P.M. to A.M. ratio was variable but then settled down to about a factor of 2 for the week prior to the balloon flight. Possible reasons for the variability of this ratio are given later.

Measurements by Syed and Harrison [1981a] from Calgary (51°N, 114.1°W, about 325 km southwest of Cold Lake) are also given in Figure 21. Where the observation dates coincide, there is good agreement between the measurements except on February 12. The agreement would imply that the air sampled above the two observation sites had a common source origin.

Near February 27 a major stratospheric warming occurred and the polar vortex split into two low-pressure centers. By February 27, one low was situated almost over Calgary, and the other at 75°N, 50°E. During this time, Syed and Harrison [1981a] observed a decline in evening NO₂ to values similar to those observed at the beginning of February. The evening abundances reported by Noxon *et al.* [1979b] for the same air mass are about a factor of 2 lower. Some of this discrepancy is again due to the choice of different twilight enhancement factors. It is unfortunate that Syed and Harrison do not report morning abundances, but the data of Noxon *et al.* [1979b] indicate a diurnal change of at least 1.5. Thus prior to the balloon flight the air feeding the stratosphere above Cold Lake and the air confined to the original polar vortex contained a constituent capable of releasing active NO_x during the daylight period.

TABLE 3. Rate Processes

Reaction Number	Reaction
(R1)	$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$
(R2)	$\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$
(R3)	$\text{NO}_2 + h\nu \longrightarrow \text{NO} + \text{O}$
(R4)	$\text{NO}_2 + \text{O}_3 \xrightarrow{\text{M}} \text{NO}_3 + \text{O}_2$
(R5)	$\text{NO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$
(R6)	$\text{NO}_3 + h\nu \longrightarrow \text{NO} + \text{O}_2$
(R7)	$\text{NO}_3 + h\nu \longrightarrow \text{NO}_2 + \text{O}$
(R8)	$\text{N}_2\text{O}_5 + h\nu \xrightarrow{\text{M}} \text{NO}_2 + \text{NO}_3$
(R9)	$\text{HO} + \text{NO}_2 \longrightarrow \text{HNO}_3$
(R10)	$\text{HNO}_3 + h\nu \longrightarrow \text{HO} + \text{NO}_2$

DISCUSSION

A principal objective of these experiments was to assess the seasonal variation in the altitude profiles of some of the odd nitrogen species at more northern latitudes. Apart from possible differences in the abundance of total odd nitrogen, seasonal differences were expected for several reasons. The rates of many chemical reactions are significantly changed owing to normally lower winter temperatures and enhanced concentrations of O_3 at lower altitudes. Photochemical processes, including radical generation, are greatly reduced owing to lower insolation and the shortness of the day. For example, in mid-August at 51°N the daylight period is almost 14 hours and the minimum zenith angle is about 40° , whereas in mid-February at 54°N the daylight period is only 9.5 hours and the minimum zenith angle is as large as 67° . In summer the stratospheric easterly flow is comparatively weak and the air mass undergoing observation has spent several days in regions of approximately constant average insolation so that there is a high probability of the odd nitrogen species having achieved photochemical steady state. In winter, with the development of planetary waves, the flow is usually much stronger and less stable. The low-pressure polar vortex seldom survives for a period longer than a few weeks before high pressure developments perturb the vortex pattern. Also, at least over North America, the vortex flow is seldom very zonal. Thus a sam-

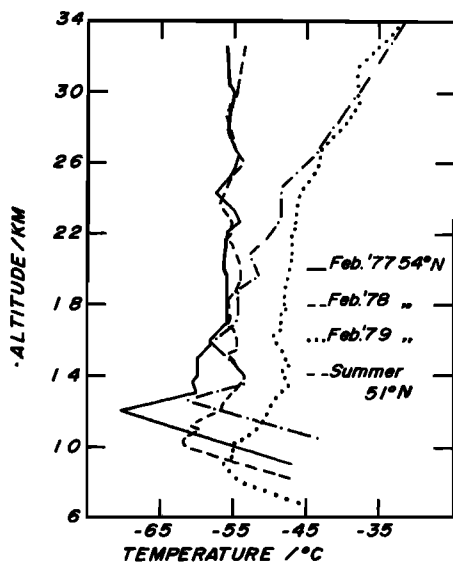


Fig. 22. A comparison of the temperature distributions for the three winter flights and one from 51°N in summer.

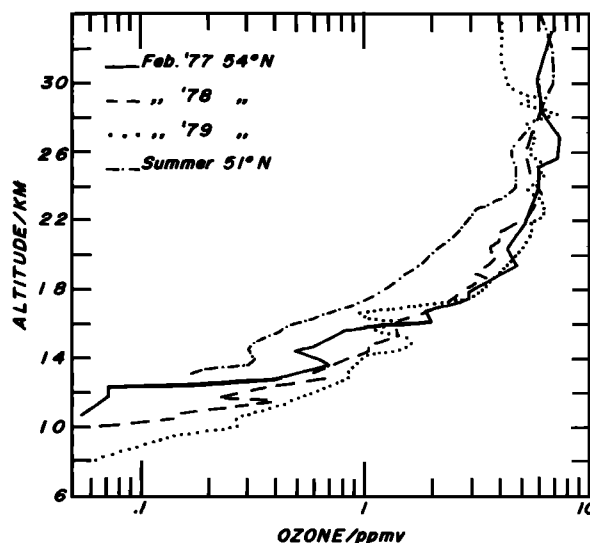


Fig. 23. A comparison of the ozone mixing ratios measured closest in time to the odd-nitrogen measurements for the three winter flights and one from 51°N in summer.

pling site in the 54°N region may be strongly influenced by the polar region that experiences no or very little insolation. The concentration of odd nitrogen species with photolysis time constants comparable to advection times would then depend upon the previous residence time at high latitudes and upon the transit time to the observation site [Solomon and Garcia, 1983a, b; Knight *et al.*, 1982]. The profiles of species like HNO_3 that have much longer photolysis time constants may then be unrelated to simultaneously measured species with much shorter time constants. It is therefore probable that many of the odd nitrogen species in the air mass under observation would not be in steady state in winter.

We shall divide the discussion into two sections. The first part will consider the observations in winter and summer without regard to transport. That is, we shall assume the flow in the 50° – 60°N region to be truly zonal and consider the expected seasonal differences on the basis of current chemistry. The second section will discuss qualitatively the influence of transport processes.

Rate processes referred to in this section are summarized in Table 3.

Winter/Summer Photochemical Variations at 51° – 54°N

We begin by examining the seasonal differences in the altitude profiles of NO_x at 51° – 54°N . The winter NO_2 profile was not measured in the program, so its value must be estimated from the NO_2/NO steady state ratio, namely,

$$[\text{NO}_2]/[\text{NO}] = k_1[\text{O}_3]/J_{\text{NO}_2} \quad (3)$$

where J_{NO_2} is the photodissociation coefficient for (R3). This approach should be valid and of sufficient accuracy for this discussion because the time constant for the photochemical exchange between NO and NO_2 during the day is only a few minutes and the chemistry should be dominated by (R1) and (R3). We have assumed that the abundance of radical species such as HO_2 and ClO are insignificant because of the low insolation. Contingent upon the validity of this chemistry we can demonstrate that the observed wintertime profile of NO implies a reduction in NO_x and not solely a shift in the partitioning of NO_x .

Figures 22 and 23 summarize the temperature and O_3 dis-

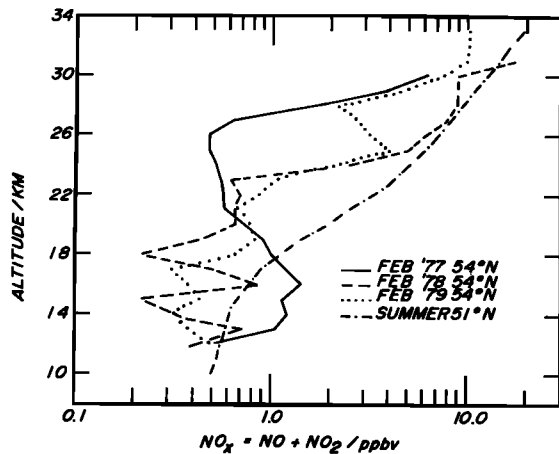


Fig. 24. The calculated abundances of $\text{NO}_x = \text{NO} + \text{NO}_2$ for each winter flight compared with the observed summer average at 51°N .

tributions measured closest in time to the large balloon flights along with the summer distributions at 51°N . There are considerable differences in the vicinity of the tropopause regions, but above 14 km and up to 29 km the winter O_3 distributions are similar and much larger than in summer up to 25 km. The winter 1977 and 1978 temperature distributions are also very similar above 14 km and normal for this latitude. The summer and normal winter temperatures do not depart greatly until about 21 km. Thus in the 14- to 21-km region, decreased average insolation, increased O_3 , but similar temperatures, shift the wintertime partitioning of NO_x to favor a larger fraction existing as NO_2 . For the 1979 winter warming case, increased temperature in the 14- to 21-km region amplifies this shift to NO_2 . This is in qualitative agreement with the observation of lower NO on average at lower altitudes in February 1979. Above 21 km, during normal wintertime conditions, the effects of enhanced O_3 and decreased insolation are offset by the reduction in temperature. Qualitatively, the expected change in NO from summer to winter conditions due to changes in NO_x partitioning is a reduction below about 21 km. The 1978 and 1979 winter observations indeed show such a reduction.

However, the winter NO_x distributions as calculated from the observed NO and (3) also show a reduction. These are shown in Figure 24. The O_3 and temperature distributions were taken from Figures 22 and 23 and J_{NO_2} was calculated from a multiple scattering routine appropriate to the temperature and zenith angle of the NO observations. A surface albedo of 25% was assumed [Madronich, 1982]. Included in the figure is the high-sun NO_x summertime distribution determined by summing the observed average NO and NO_2 distributions for 51°N . Although there are marked differences between the calculated winter NO_x distributions, there is a significant wintertime reduction in NO_x at all altitudes and hence in the NO-derived total column abundance. The decrease in NO_x implied by the observed NO distribution is also consistent with the wintertime reduction in column NO_2 deduced from aircraft and ground-based methods.

The peak in calculated NO_x near 15 km in 1977 reflects the observed peak in NO and may be less common in winter. For example, Noxon [1979] and Syed and Harrison [1980] usually observed the center of mass of the NO_2 column to be between 25 and 30 km. In February 1977, Noxon observed the center of mass to be unusually low at 20 km. This could be explained

as resulting from averaging the high- and low-altitude maxima of Figure 24.

The reduction in NO_x could have resulted from a net reduction of NO_y at northern latitudes in winter. If, on the other hand, poleward and downward transport caused a net increase in NO_y in winter, as is observed for O_3 , then the winter reduction in NO_x would be even larger than shown in Figure 24. For example, if the O_3 distributions of Figure 23 were plotted in relation to the average summer or winter tropopause altitude, the distributions would coincide. This would amount to lowering the summer curve of Figure 23 by 2–3 km at all altitudes. A similar treatment for observed NO and calculated NO_x would amplify the seasonal change of these species. Furthermore, the Solomon and Garcia [1983a] model gives about a 25% increase in NO_y from 16 to 23 km in winter compared with summer at 54°N (S. Solomon, private communication, 1983). Thus there is ample evidence that NO_x is indeed reduced at all altitudes below about 30 km.

An immediate question is to which reservoir species has NO_x been converted in winter. Possible candidates are HNO_3 , HNO_4 , ClONO_2 , or N_2O_5 or that heterogeneous processes constitute a net northern winter sink for odd nitrogen. Noxon [1979] had suggested earlier that HNO_3 was the likely reservoir species, though recently Noxon et al. [1983] supported a more important role for N_2O_5 . Evans et al. [1982] concluded that heterogeneous conversion of NO_x to HNO_3 at low altitudes would not be inconsistent with their data. Both Knight et al. [1982] and Solomon and Garcia [1983a, b] favored N_2O_5 as the dominant winter reservoir species. We shall offer further evidence for the case of N_2O_5 in a later section. But first we will examine the data to see if they suggest NO_x to HNO_3 conversion. Because HNO_3 is observed to be the dominant NO_y species both in winter and summer below 25 km, only a small fractional increase in HNO_3 is required to produce a large fractional decrease in NO_x . Because of the limited data set, it is expected to be difficult to determine unequivocally the magnitude of possible NO_x to HNO_3 conversion in winter.

Figure 25 shows the altitude distributions of the sum of HNO_3 , NO_2 , and NO. The two summer profiles, one formulated using the average HNO_3 distribution and the other formulated using the single Yorkton 1976 profile of Figure 1, are significantly different only at the lowest altitudes. Apparently,

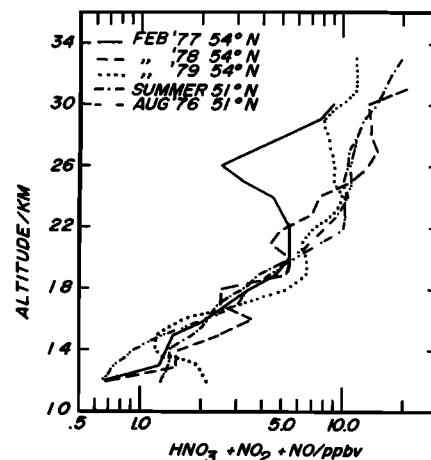


Fig. 25. The sum of NO, HNO_3 , and calculated NO_2 for each winter flight compared with the summer average at 51°N and with the observed sum at Yorkton in August 1976 [Evans et al., 1981].

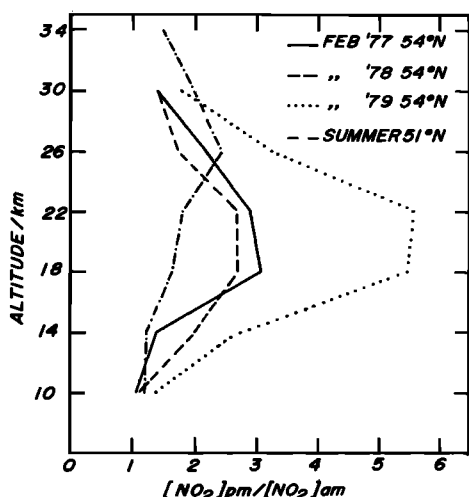


Fig. 26. The expected ratio of evening NO_2 to morning NO_2 for the measured temperature and ozone conditions of each winter flight compared with a similar calculation for summer. The calculation was done at 4-km height intervals.

a larger range of values are possible in summer at lower altitudes. The winter distributions were determined from the observed NO and HNO_3 . NO_2 was calculated using (3).

In summer at this latitude models [cf. *World Meteorological Organization*, 1981] indicate that NO , NO_2 , and HNO_3 are the dominant NO_y species so that the summer curves of Figure 25 can be considered a reasonable approximation of NO_y . Thus if NO_y were conserved between the seasons, the similarity of the summer and winter curves of Figure 25 for 1979 and below 20 km for 1977 and 1978 would suggest that conversion of NO_x to HNO_3 would be sufficient to account for the winter reduction deduced for NO_x . Above 22 km the 1977 and 1978 distributions would imply that this conversion was insufficient and that an additional reservoir species must have been present.

However, and as discussed previously, it is likely that NO_y builds in the northern winter stratosphere as does O_3 . In order to observe such an enhancement more clearly, the data should be referenced to the average tropopause heights for each season. This would require a displacement of the summer values of Figure 25 downward by 2–3 km. The resulting summer NO_y would then be larger than the sum of winter NO_x and HNO_3 . One would then conclude that HNO_3 is not a sufficient reservoir to account for the reduction of NO_x in winter. However, until the magnitude of the winter NO_y increase is verified by measurements, we cannot estimate the amount of conversion of NO_x to HNO_3 from our data.

There are two further arguments against HNO_3 being the sole winter reservoir of NO_x . First, the photolysis time constants in the altitude region where HNO_3 is most abundant are much too long to explain either the observed diurnal variation of NO_2 or to account for the rapid growth in NO_2 or NO_x as the cliff is traversed to lower latitudes. Second, as discussed previously by *Noxon* [1979], the homogeneous production rate of HNO_3 by (R9) is reduced at this latitude because reduced insolation decreases the OH concentration. Our one-dimensional model predicts the steady state OH abundance to be a factor of 6 lower at 14 km in comparison with summer insolation conditions. The situation is even worse if the air mass resided for any length of time at more northern latitudes.

Of the remaining possible wintertime reservoirs of NO_x

both our one-dimensional model and the two-dimensional model of *Solomon and Garcia* [1983a] predict that HNO_4 and ClONO_2 are considerably less abundant than N_2O_5 . Although HNO_4 and ClONO_2 are more stable at the low normal winter temperatures, both are believed to require photolytically generated radical precursors for their formation, and the comments made above concerning HNO_3 production via OH also apply. However, *Stockwell and Calvert* [1983] have recently proposed that HO_2 may be formed at night by the reaction of NO_3 with formaldehyde. Thus it is possible that HNO_4 could build in the darkened northern winter stratosphere if sufficient formaldehyde or similar compounds reach the stratosphere. Because further information is required to verify the importance of this proposal for the stratosphere, we shall concentrate upon the evidence that N_2O_5 is a likely major NO_x reservoir in winter at northern latitudes.

The role of N_2O_5 . *Knight et al.* [1982] favored N_2O_5 as the major winter reservoir of NO_x because (1) it can account for the observed diurnal variation in the column abundance of NO_2 in winter at 54°N , (2) it is qualitatively consistent with the rapid growth in NO_2 equatorward of the cliff, and (3) a cursory examination of the stratospheric flow for the February 1979 flights indicated that the air mass sampled resided for 3–4 days at latitudes well north of Cold Lake where the low average insolation would favor NO_x to N_2O_5 conversion. Subsequently, the model of *Solomon and Garcia* [1983a] predicted a strong poleward increase in N_2O_5 in winter. The cliff was also reproduced quite well, although a calculated diurnal variation of column NO_2 of 1.5 at 54°N significantly exceeded *Noxon's* [1979] observation.

If we consider N_2O_5 to be a major winter reservoir of NO_x , we can use our data to examine further the interconversion of NO_x and N_2O_5 . Our ground-based measurements of NO_2 illustrate that a diurnal variation was observed above Cold Lake in 1977 and 1979. From our previous discussion it is likely that one also occurred in 1978. We can then examine what our measured altitude distributions and the assumed chemistry of Table 2 would predict to occur. For the moment, we shall continue to assume an air mass confined to strict zonal flow in the 50° – 60°N region for a period of 2–3 days, one in which NO_x and N_2O_5 have achieved steady state.

At steady state the nighttime formation of N_2O_5 via (R4) and (R5) must balance the daytime photolysis, (R8). Then the ratio of the NO_2 concentration in the evening compared with the morning, both when the solar zenith angle is 90° , is given by

$$[\text{NO}_2]_{\text{P.M.}}/[\text{NO}_2]_{\text{A.M.}} = \exp(2k_4[\text{O}_3]\Delta t_n) \quad (4)$$

since (R4) is rate limiting. Here Δt_n is the duration of the night, and it is assumed that O_3 and temperature remain the same over the 24-hour period. Figure 26 shows the expected steady state distribution of the NO_2 ratio calculated from (4) for the observed conditions of O_3 and temperature encountered during both the winter flights ($\Delta t_n = 14.5$ hours in mid-February) and the summer flight at Yorkton ($\Delta t_n = 10$ hours in late August). When the winter temperatures are normal, the longer winter night and enhanced O_3 contribute to a larger diurnal ratio as compared with summer up to 24–25 km. During the warming case, this trend is amplified owing to the strong temperature dependence of (R4). At higher altitudes the normally colder winter temperatures more than offset the O_3 and time effects so that the 1977 and 1978 curves fall below the summer average.

TABLE 4. Diurnal Change of Column NO₂

	Date	Latitude, °N	[NO ₂] _{P.M.} /[NO ₂] _{A.M.}	Stratospheric Flow
<i>Kerr et al.</i> [1982]	summer	51	1.7	
This work	Feb. 1977	54	1.9 ± 0.4	~ polar vortex
This work	Feb. 1978	33	1.5	
This work	Feb. 1978	40	1.7	
This work	Feb. 1978	45	1.7	
This work	Feb. 1979	54	2.1 ± 0.6	stratwarm*
<i>Noxon</i> [1979, 1980]	Feb. 1977	54	≤ 1.1	polar vortex
<i>Noxon</i> [1979, 1980]	Jan. 1978	51–54	≤ 1.1	nonvortex
<i>Noxon et al.</i> [1979a]	Feb. 1979	51	~ 1.5	stratwarm
<i>Noxon et al.</i> [1979b]	summer	40	1.7 ± 0.2	
<i>Syed and Harrison</i> [1981a]	Jan. 1979	51	2.6 ± 1.0	vortex/stratwarm
<i>Syed and Harrison</i> [1981a]	Feb. 1979	51	2.4 ± 0.8	stratwarm
<i>Syed and Harrison</i> [1981a]	Dec. 1978	51	1.5 ± 0.1	polar vortex
<i>Coffey et al.</i> [1981]	Feb. 1978	50	2.3	nonvortex
<i>Solomon and Garcia</i> [1983a]	Feb. 1977	56	1.5	calculated

*"Stratwarm" indicates stratospheric warming.

Provided NO_x/N₂O₅ steady state has been achieved, Figure 26 predicts that a diurnal change of NO₂ should be observed in winter unless all of the NO_x was situated well above 30 km. Our observed NO profiles and the calculated NO_x distributions of Figure 24 show that this was not the case. Thus we would predict a diurnal change to be observed in each year. However, none of the Cold Lake measurements were made under conditions of zonal flow nor is it likely that NO_x/N₂O₅ steady state was completely achieved. Thus we cannot calculate the diurnal ratio. Nevertheless, even if steady state was only partially achieved, some diurnal change should have been expected. This is in agreement with our ground-based observations of column NO₂.

At steady state the magnitude of the diurnal change in winter compared with summer should depend upon the vertical distribution of NO_x (cf. Figure 26). If all of the NO_x were distributed above about 26 km, the diurnal ratio would be expected to be less in winter than in summer. Conversely, if it were distributed below about 25 km, the diurnal change would be expected to be larger in winter. Table 4 summarizes observed and calculated values of the diurnal ratio of column NO₂. An indication of the type of stratospheric flow is included. There is no disagreement in the literature concerning the existence or magnitude of the diurnal ratio in summer in the 40°–55°N region. However, there are some ambiguities concerning this ratio in winter. These may be due to the following: (1) There is reduced precision of the winter measurements caused by lower NO₂ abundance, particularly in the morning. (2) The technique requires observations to be made to the southeast in the morning and to the southwest in the evening. If much of the NO₂ is near 30 km, the absorption air masses are some 300–400 km apart. Even if the stratospheric flow is nonzonal but steady, the two observations may be made on independent air masses. (3) Because 2–3 days are necessary to reach steady state, together with nonsteady flow, changes in temperature, ozone, or insolation could degrade any relation between morning and evening measurements. Indeed, the data of Figures 19 and 21 show incidences of independent trends that could be due to the above factors. Nevertheless, the entries of Table 4 suggest that the diurnal variation is lower in

winter whenever the observation site is within the polar low pressure vortex flow. It is not clear that the winter vortex ratio is significantly lower than the summer value. In winter, when the observation site is not within the polar vortex flow or when a stratospheric warming occurs, the diurnal ratio in the majority of cases is larger than both the vortex values and the summer values. Figure 26 suggests that more NO_x should then be found at lower altitudes or that the onset of the strong layer in NO (and NO_x) should move to lower altitudes. This was observed in our 1978 and 1979 profiles of NO.

In summary, the majority of the measurements, as well as the calculated value in Table 4, indicate a significant diurnal change in the winter column amount of NO₂ even during cliff and polar vortex conditions. There is strong evidence that N₂O₅ to NO_x interconversion accounts for both this variation and the reduction in winter NO_x. However, some data show little diurnal variation in column NO₂. Should further measurements confirm these observations, then the presently assumed chemical processes would have to be changed substantially. For example, N₂O₅ or NO₃ would have to be removed rapidly during the night to products which were incapable of releasing NO_x during a single daylight period.

Further evidence for the importance of N₂O₅ in the northern winter comes from the slow growth of NO near 29 km shown in Figure 7. If this is attributed to release of NO_x by N₂O₅ photolysis, an estimate of the daytime abundance can be made. Because steady state between NO_x and N₂O₅ may not have been achieved, the estimate must be considered a lower limit. During the day the NO_x released in time t_D is given by

$$\frac{\Delta \text{NO}_x}{\Delta t_D} = 2 \langle J_{\text{N}_2\text{O}_5} \rangle \langle [\text{N}_2\text{O}_5] \rangle \quad (5)$$

where $\langle J_{\text{N}_2\text{O}_5} \rangle$ is the average daytime photolysis coefficient [*Solomon and Garcia*, 1983a]. The ratio $\Delta \text{NO}_x / \Delta t_D$ may be computed from Figure 7 and (3). It gives a lower limit for the average daytime mixing ratio of N₂O₅ at 29 km of 3 ppbv. The noontime mixing ratio calculated by *Solomon and Garcia* [1983a] for 54°N and 29 km is 3.5 ppbv. The close agreement does indicate a consistent picture for the role of N₂O₅.

Influence of Stratospheric Dynamics

While consideration of N_2O_5 production and photolysis can explain the winter decrease in NO_x , the enhanced wintertime variability and strong layering of our measurements, together with the work of Noxon and co-workers [Noxon *et al.*, 1979a, b, 1983; Noxon, 1979, 1980], suggest that stratospheric dynamics plays a dominant role in determining the distribution of trace species at northern latitudes in winter.

A stratospheric flow from the darkened polar region to the observation site can conceptually account for the variability of the mixing ratios of odd nitrogen compounds. In the darkened polar region, NO is converted to NO_2 via (R1) and NO_2 to N_2O_5 via (R4) and (R5). The extent of conversion of NO_x to N_2O_5 depends upon the residence time at high latitudes, O_3 , and temperature. At lower altitudes, roughly 10–25 km, where in winter the O_3 concentration is high, almost complete conversion can occur in a few days. At higher altitudes, proportionately longer times are required, as O_3 is less abundant. Moreover, wind speeds at high altitudes are usually greater (cf. Figures 11 and 16), thus shortening the residence times at high latitudes and the extent of conversion. The daytime abundance of NO_x upon transport of this air mass to a more southern location is then dependent upon the extent of conversion, the rate of NO_x release from N_2O_5 , and the time the air mass has spent in daylight. If the large-scale flow pattern were also to change, then this picture would be complicated by the infusion of air masses from different latitudes or even different altitudes.

Even a cursory examination of the National Meteorological Center (NMC) upper air charts for the northern hemisphere winter reveals that the stratospheric circulation is not very stable over an extended period of time. Indeed the balloon flights sampled three different isobaric systems, and we will attempt to relate the changes in these stratospheric conditions to the three sets of observations. Only in 1977 do the NMC charts indicate a reasonably stable pattern for almost a week prior to the balloon flight. Because of this stability we were able to make a crude analysis of the likely source of the air that was sampled during the flight. In 1978 and 1979 the pressure patterns are either very complex and/or unstable, and it is unrealistic to determine air mass trajectories from a simple analysis of the pressure contours. A proper analysis based upon isentropic trajectories [Danielsen, 1961] is required but is beyond the scope of this paper.

1977. There are several features of the observed altitude profiles of February 19, 1977, that are examined in relation to the stratospheric flow: (1) low HNO_3 as compared with both the profiles of February 1978 and 1979 and the column abundance determined from the aircraft latitude surveys; there was also a layer of enhanced mixing ratio above 26 km; (2) the N_2O and fluorocarbon profiles exhibited a folded distribution; (3) the NO profile showed a double-peaked distribution.

Noxon [1979] reported that cliff conditions were established before and after the balloon flight and that Cold Lake was north of the cliff throughout the period of the balloon campaign.

We have examined the NMC charts from February 1 to February 20 from 200 to 10 mbar. Some of these charts are shown in Figures 27 and 28. Up until February 9 the pattern of circulation was unstable, whereas from February 10 to 19 the pattern stabilized. For our qualitative purpose the source of the air mass sampled could then be approximated from the pressure contours. At 10 mbar (~31 km) the rapid circulation

north of 50° was generally nonzonal, and so the air masses that arrived over Cold Lake were likely not in photochemical steady state for NO_x/N_2O_5 interconversion.

At 10 mbar on February 1 there was an extensive polar low-pressure region where anticlockwise flow was very elongated so that the flow traversed the pole directly from the eastern hemisphere to the Cold Lake region. By February 5 the low had intensified, and through February 19 the low- and high-pressure system gradually rotated anticlockwise about the pole (cf. Figure 25). Throughout this period, Cold Lake was within the strong low-pressure flow at 10 mbar and received air that traversed the polar region above $70^\circ N$, mostly from the region of continuous darkness at latitudes above $76^\circ N$. The transit time for an air parcel to move from $55^\circ N$ in the eastern hemisphere over the polar region to Cold Lake was estimated at approximately 2 days.

At 30 mbar the flow was similar to that at 10 mbar from February 1 to 5. By February 10, Cold Lake was outside the polar vortex flow, and the flow reaching Cold Lake was much weaker and originated from the 35° – $45^\circ N$ region (cf. Figure 25). This basic pattern continued through February 19, but a more distinct wave developed over the west coast of North America that carried mid-latitude air north over Alaska and then south to Cold Lake. Air that arrived at Cold Lake did not likely travel much north of $65^\circ N$ but had spent a lengthy time at mid-latitude. Because the flow was weaker at 30 mbar, the transit time through the wave features from $55^\circ N$ to $65^\circ N$ and back to $55^\circ N$ was still just over 2 days.

The situation was similar at all lower altitudes down to 200 mbar (cf. Figure 28). From February 10 onward, the flow pattern was quite stable and the source region for Cold Lake air parcels was from nearly zonal flow (except over North America) at the position of the jet stream between 30 and $50^\circ N$. By February 18 and 19 the wave feature over northern British Columbia and Alaska intensified at the lowest altitudes such that Cold Lake was south of the jet core on February 19, as discussed earlier. It was the change in this wavelike flow that caused the trend to more northerly flow observed from the sondes at Primrose Lake (cf. Figure 11). Estimates of the transit time from $55^\circ N$ and west of the North American coast northward to $65^\circ N$ and back south over Cold Lake were 1, $1\frac{1}{2}$, 2, and 2 days at 200 mbar (~11 km), 100 mbar (~16 km), 70 mbar (~19 km), and 50 mbar (~21 km).

Therefore during the 9 days prior to the balloon flight, air that arrived over Cold Lake had two distinct source regions. At 10 mbar the air was of polar origin or at least had spent several days traversing the darkened polar region. At and below 30 mbar the air originated from and resided a considerable time at mid-latitudes. Obviously, between 30 mbar and 10 mbar the air was very likely a mixture of polar and mid-latitude air.

This analysis gives a consistent picture for the February 1977 HNO_3 vertical distribution. For altitudes below 10 mbar the transit time through the wave feature over the west coast of North America was less than the lifetime of HNO_3 . Consequently, the distribution of HNO_3 reflected its mid-latitude origin where the mixing ratios are believed to be low. Above this altitude, HNO_3 was likely of polar origin where the aircraft latitude survey and satellite measurements referred to earlier support enhanced levels in winter. Thus it is possible that the enhanced layer of HNO_3 above 26 km of Figure 1 marked the transition region that separated mid-latitude from polar vortex air. However, until a detailed trajectory analysis

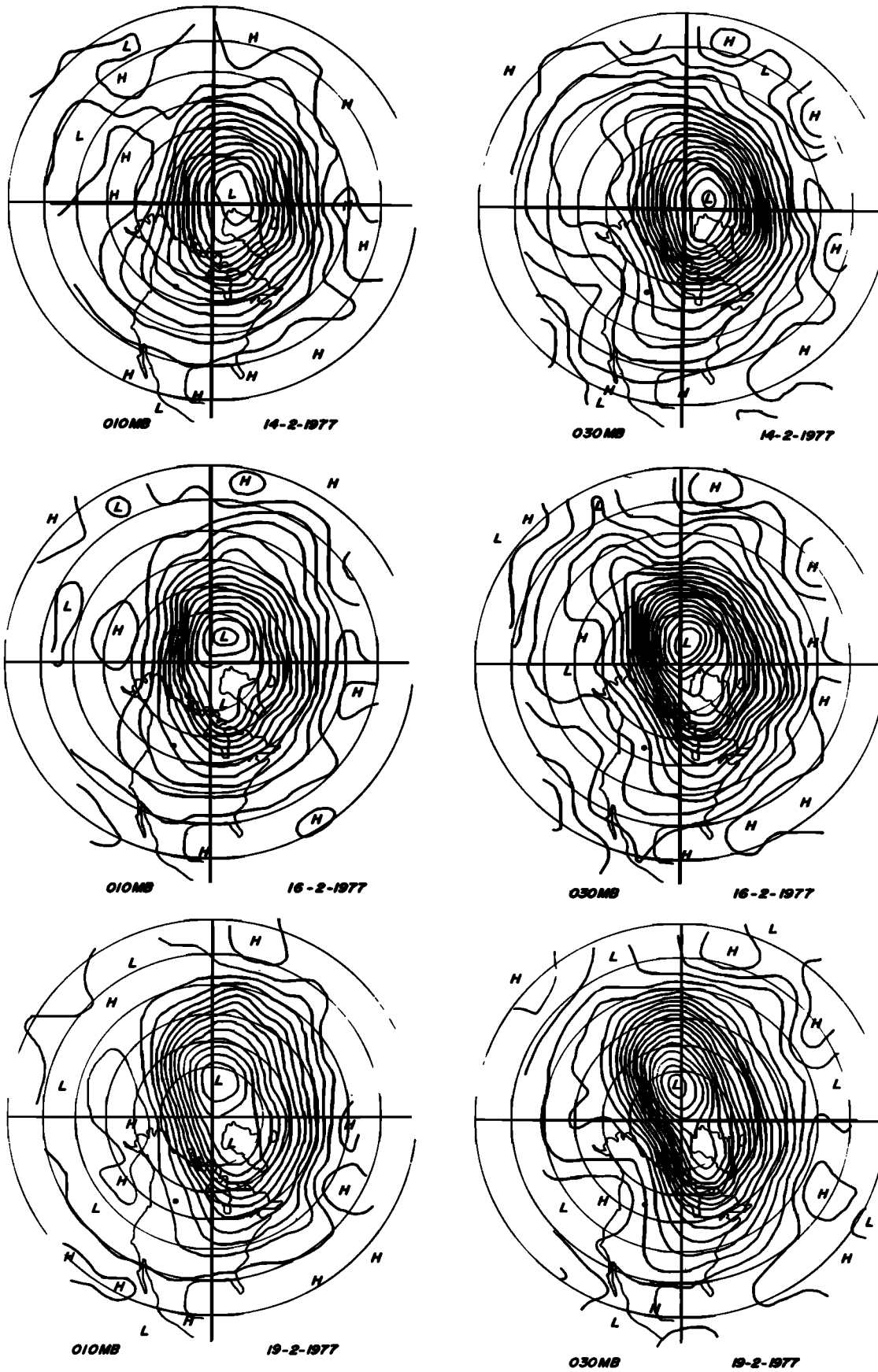


Fig. 27. NMC charts at 10 mbar (~31 km) and 30 mbar (~24 km) for February 1977

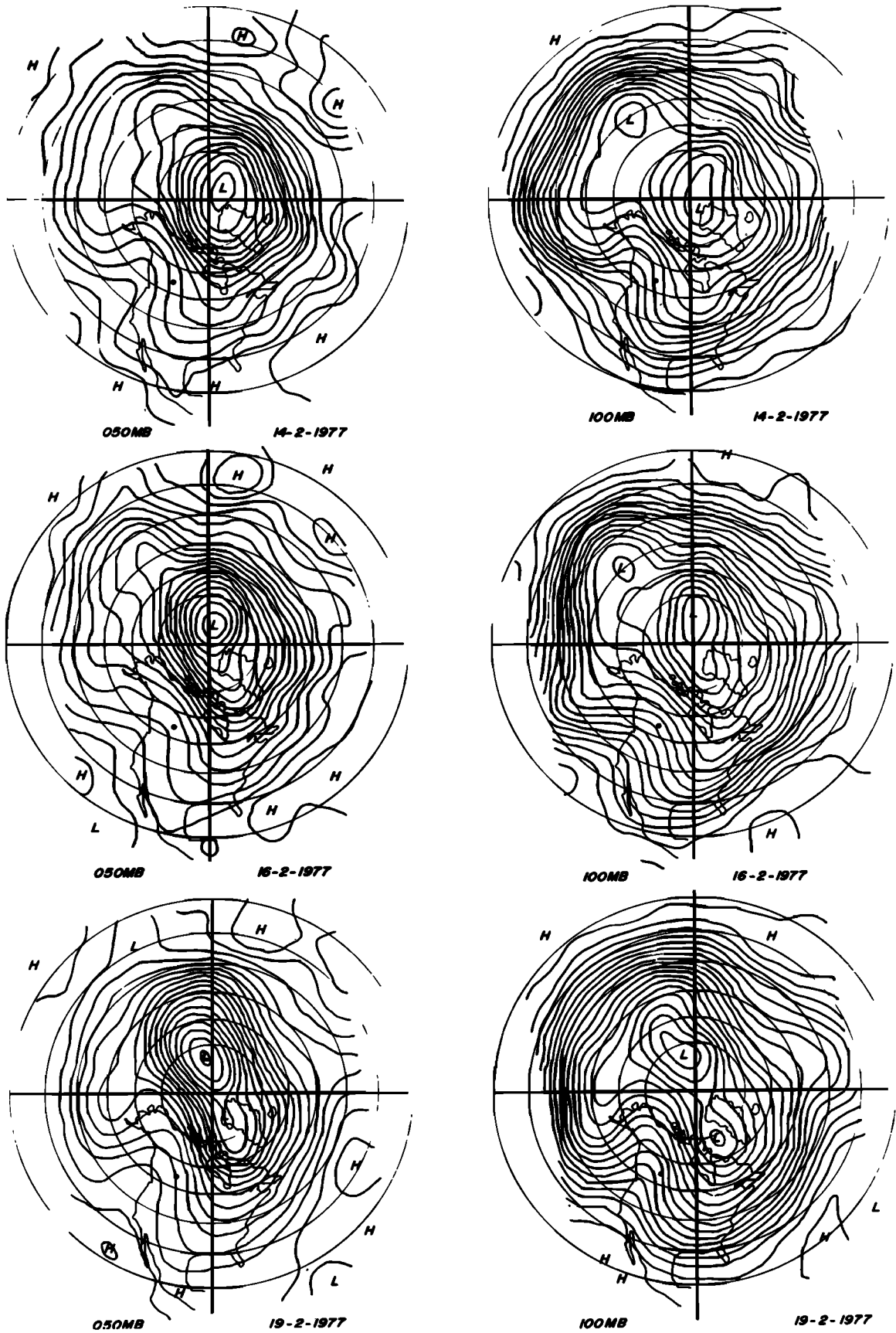


Fig. 28. NMC charts at 50 mbar (~21 km) and 100 mbar (~16 km) for February 1977.

is made for several weeks prior to February 19 some caution should be attached to this interpretation. The polar vortex at 10 mbar was quite elongated for the week prior to the flight such that the flow that traversed Cold Lake reached as far south as 40°N over North America and in the opposite hemisphere. Thus the air parcel spent a considerable time at southern latitudes where the photolysis lifetime of HNO_3 is about 1 to 1.5 days at 30 km between 40° and 50°N. Unless the air mass is traced back to a long duration in the polar region, this interpretation may be oversimplified.

A reason for being cautious in the above rationalization of the 1977 HNO_3 distribution stems from the N_2O and fluorocarbon observations of Figure 8. In summer one would expect smaller mixing ratios of these species in the sunlit polar region due to photolysis of these species in the slow northward transit from the equatorial Hadley cell. Indeed the two-dimensional models of the *World Meteorological Organization* [1981] report predicted a summertime increase in the vertical gradient of these species between mid-latitudes and the pole. In winter one would expect the mixing ratios to change little if the species remain confined to the polar region. Thus on the basis of the air below 26 km originating from mid-latitudes we would have expected mixing ratios comparable to summer values near 50°N. This is in reasonable agreement with our observations if the summer and winter values are referenced to the tropopause. However, if the air above 26 km had been confined to the polar region from the summer/fall season, much lower than observed mixing ratios would have been expected. Consequently, to rationalize the observations, the air sampled above 26 km during the balloon flight must have been of polar duration long enough for nitric acid to build but ultimately must have originated from lower latitudes where the mixing ratios of N_2O and CMF's are larger. Because the lifetimes of these species are very long, air mass trajectories would have to be traced back several months or so to determine the ultimate origin. Indeed, Schmidt [1982] has recently correlated folded distributions of N_2O with air mass trajectories. One anomaly in particular was an N_2O profile measured from Wyoming on February 1, 1979, by Goldan et al. [1980] that showed higher than expected mixing ratios above 23 km as well as a folded distribution even though the air mass resided for 3–4 days near the pole. Schmidt traced the air parcel over a 1-month period to the 30°N region where mixing ratios are greater. The low-latitude distribution was essentially frozen owing to the long lifetime of N_2O . The rationalization of our observed profiles might be similar.

Correlating the February 1977 NO profile with the stratospheric circulation is also more complex. At high altitudes, between 30 mbar and 10 mbar the air was from within the polar low-pressure vortex and traversed the polar region in about 2 days. As measurements on this air mass began about 1000 on February 19, the bulk of the transit time from 120°E, 50°N was spent in darkness. We estimate, using an O_3 abundance at 29 km from Figure 10 and temperatures from the NMC map (–45° to –60° in the region traversed) that at least 60% of the NO_x should have been converted to N_2O_5 . Even though NO_x partitioning favors NO at this altitude and NO_y is increased in winter, we would expect NO to be lower than in summer as was observed. At lower altitudes, say, 50 mbar (~21 km), the air originated from mid-latitudes, but because of the 2-day residence time in the wave and because the measurements were made in the morning, much of the transit time is spent in the dark or at least under conditions of

very low average insolation. Both average temperature and O_3 concentration are much higher during this wave transit than in the polar region, and we calculate a 90% conversion of NO_x to N_2O_5 . At 200 mbar the wave transit time and O_3 concentration are lower and the conversion to N_2O_5 is down to about 50%. Thus even though the air mass below 30 mbar is not from the polar vortex, the column abundance of NO_2 at Cold Lake would still be expected to be lower than in summer due to conversion to N_2O_5 .

The above arguments are qualitatively consistent with the observed distribution of NO and strengthens the argument that N_2O_5 is an important temporary reservoir of odd nitrogen. A considerably more detailed and refined calculation of the expected NO distribution for February 1977 has been performed by Solomon and Garcia [1983b] using their two-dimensional model combined with an approximate trajectory analysis. They predicted a distribution similar to that observed including a layer at the lowest altitude of their model, namely, 16 km. Thus it would appear that with a proper treatment of transport that includes diurnal changes along the trajectory, along with N_2O_5 chemistry, one can account rather well for the NO distribution. Their analysis, however, does not consider vertical motion. The temperature profiles of Figure 9 show that vertical motion in the lower stratosphere may have been important during the time of the balloon flight. The temperature lapse rate was almost adiabatic as the jet meander passed over Cold Lake. This would indicate a vertical motion of possibly 2–3 km and with some motion to at least 16 and 17 km, since there was a cooling observed to this level. The effect of this on the production of the low-altitude peak in NO has not yet been determined but certainly adds another complication to the interpretation.

1978. Figures 29 and 30 give abbreviated versions of some of the NMC charts prior to the balloon flight. From at least February 1 to 4, Cold Lake was within a very well developed polar low-pressure vortex at all altitudes between 200 mbar and 10 mbar consistent with Noxon's [1979] observation that a cliff had reformed at the end of January following the subsidence of a mild stratospheric warming. By February 6 the low was elongated east-west and the isobars suggest the flow in the 200- to 70-mbar region to have been more from mid-latitudes. Between 50 mbar and 70 mbar, Cold Lake was still within the vortex feature whose center had shifted to almost due north of Cold Lake at 70°–75°N. From February 7 onward the vortex split into two low-pressure centers at the lower altitudes. This splitting propagated slowly upward, finally reaching 10 mbar on February 13. At the same time a high developed and intensified over the Yukon so that prior to the balloon flight on February 14 the northern hemisphere was dominated by a triad of pressure systems as shown in Figures 29 and 30. At 200 mbar the circulation pattern was unusually complex with very weak flow between 50° and 70°N entirely around the globe and the jet stream was near 30°N over North America.

In contrast to the week before the 1977 balloon flight, the isobaric maps indicate dramatic flow changes in February 1978. Consequently, it is not possible to determine trajectories from a rudimentary analysis of the pressure contours. Figures 29 and 30 show that the flow north of Cold Lake underwent a considerable deceleration. Figure 11 shows that the wind speeds over Cold Lake were indeed light up to 33 km so that air mass trajectories would likely cross the pressure contours (E. F. Danielsen, private communication, 1982). Thus a detailed trajectory analysis would be required to determine

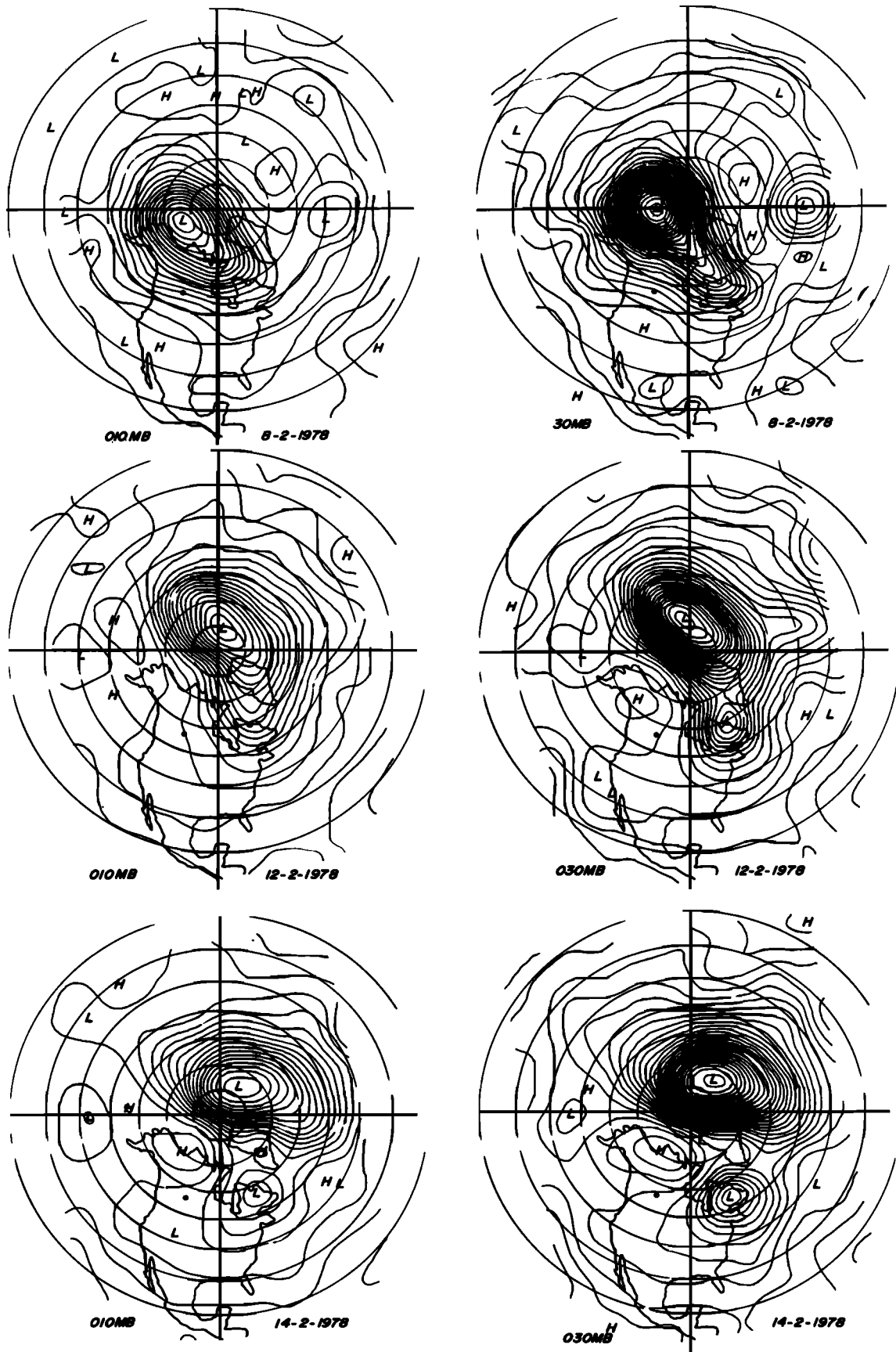


Fig. 29. As in Figure 27 for February 1978.

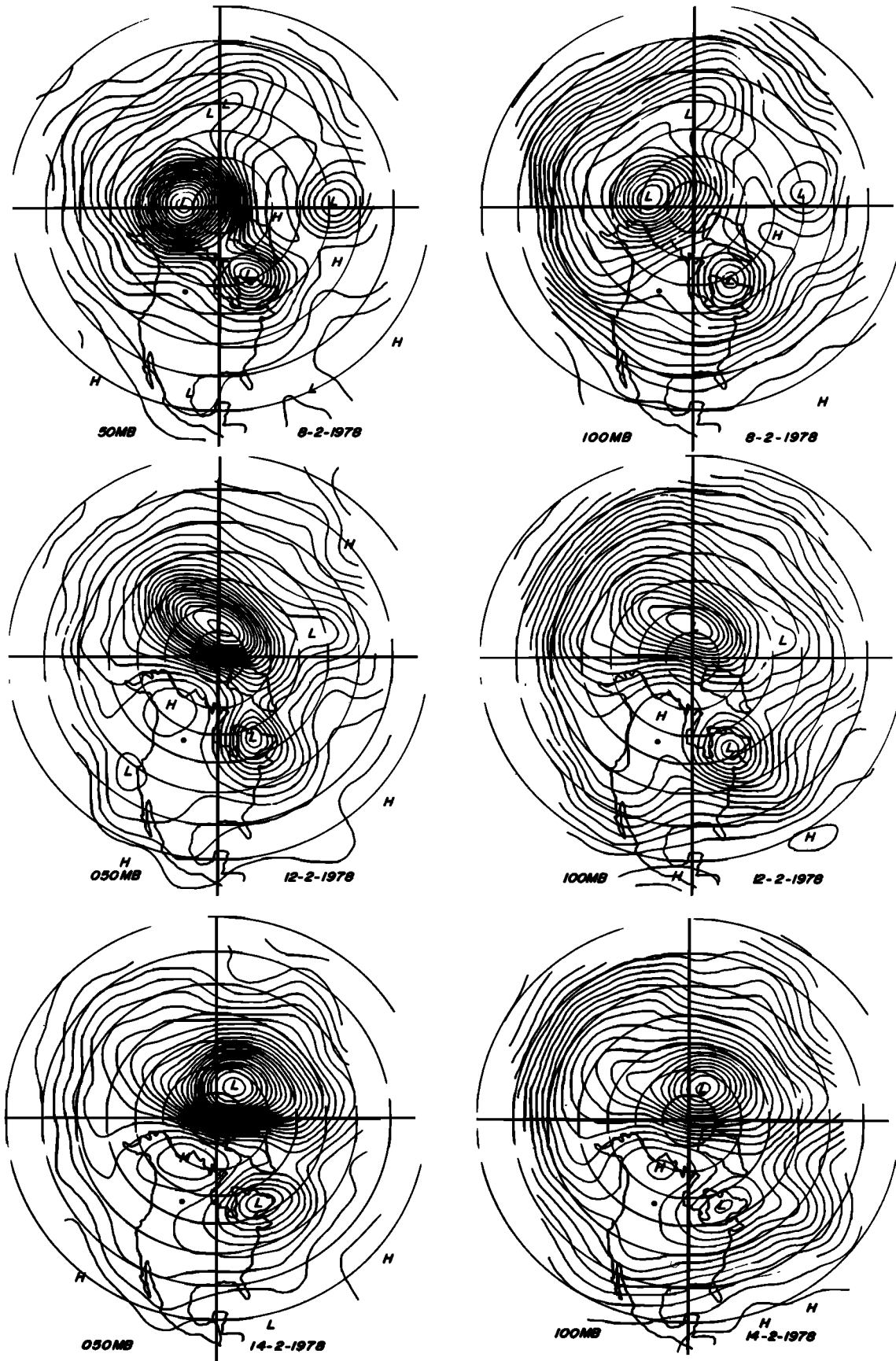


Fig. 30. As in Figure 28 for February 1978.

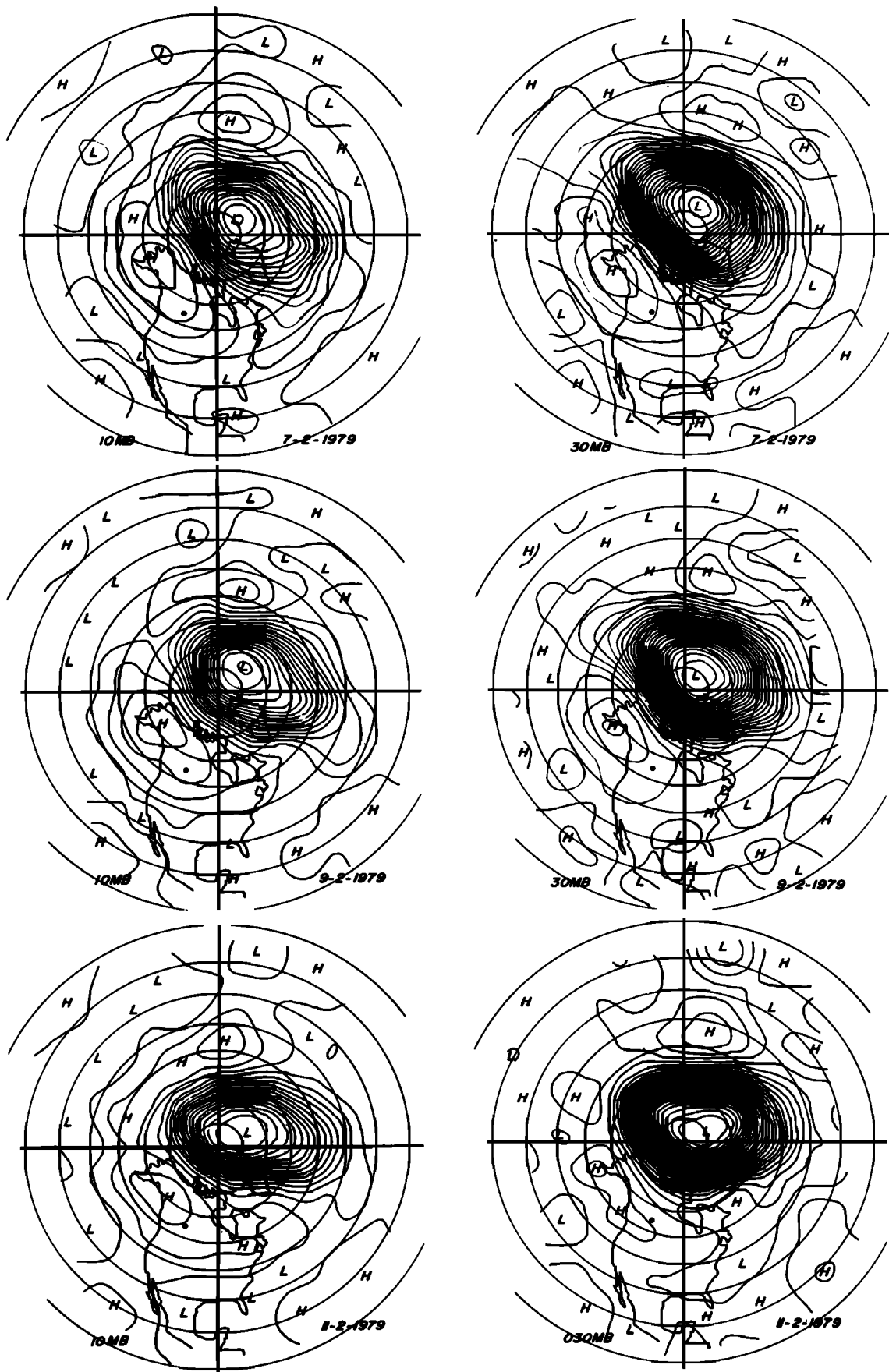


Fig. 31. As in Figure 27 for February 1979.

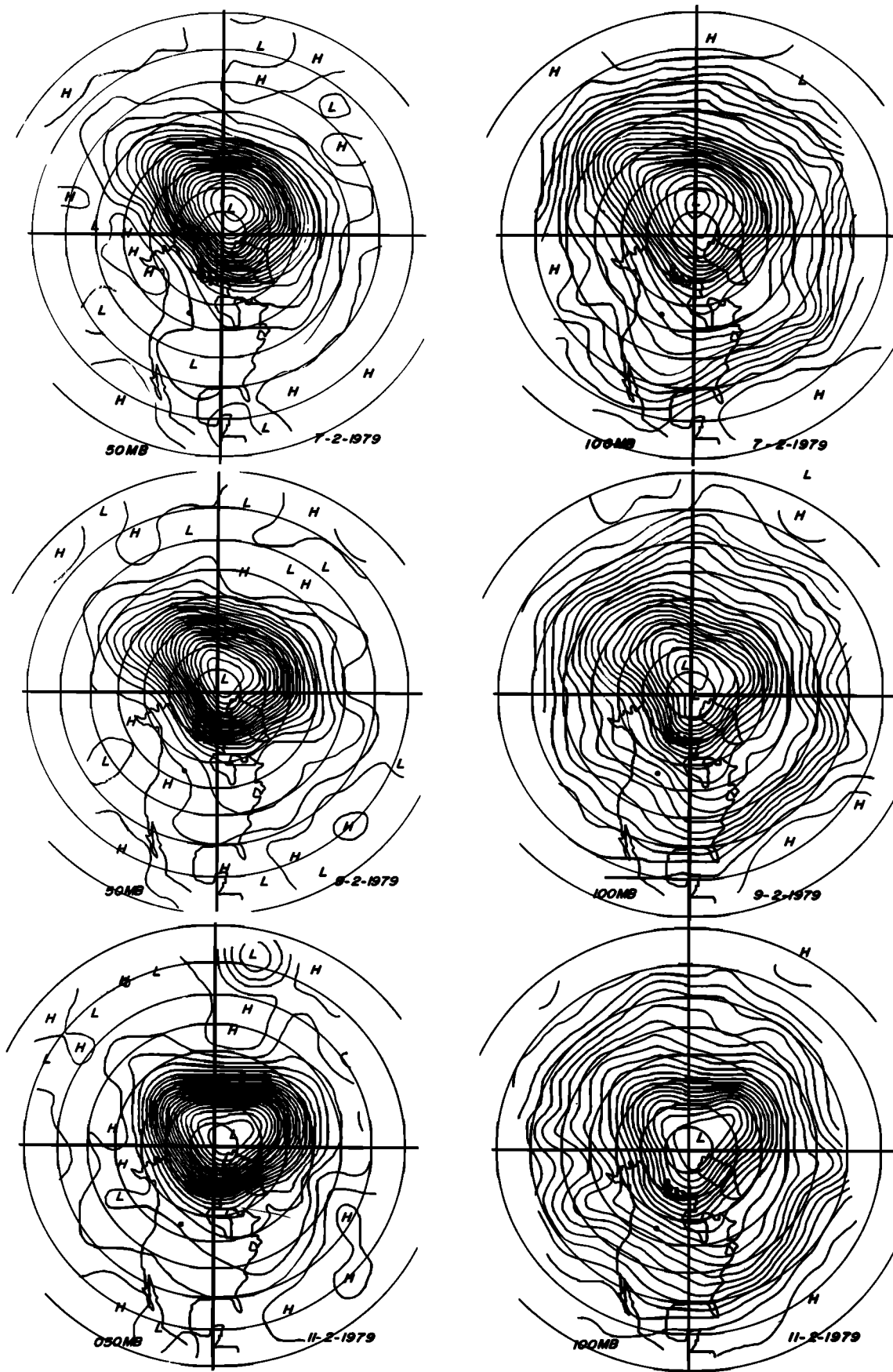


Fig. 32. As in Figure 28 for February 1979.

whether air arriving over Cold Lake was from within the larger segment of the original polar vortex or from lower latitudes via the polar region driven by the high-pressure system. Such an analysis is beyond the scope of this paper. The NMC maps do indicate that wintertime variability in the northern hemisphere in both transport and species abundance should be expected. The pressure pattern of Figures 29 and 30 is not atypical in winter.

Even though the lack of trajectory information makes analysis of the 1978 data almost impossible, we can try to rationalize some of the observations. If the air mass sampled on February 14 was polar, perhaps from the larger low-pressure vortex in Figures 29 and 30, then almost complete conversion of NO_x to N_2O_5 would have occurred because the vortex had been formed at least since the first of the month. Even if the flow was from 60°N around the high-pressure region to Cold Lake at any altitude between 100 mbar and 10 mbar the transit time would have been at least 3 days and the air temperatures in the range -50°C to -60°C . As for 1977, such a transit would have caused most of the NO_x to be converted to N_2O_5 with lesser conversion at the highest altitudes. The NO distribution at Cold Lake would then depend on which actual trajectory or combinations of trajectories and their associated insolation were suffered during the southward motion to Cold Lake. The NO mixing ratio below 23 km was extremely low, which supports a polar region transit at least at these altitudes. Although we do not have any observations of column NO_2 at Cold Lake, we would infer from Figure 18 that it was at least as low as in 1977 and considerably lower than in summer. This is consistent with the above argument.

At high altitudes, above 30 km, the observed NO profile in 1978 exceeds the summer average. We would have expected much lower values, especially as there were only 4 hours of sunlight available before the measurements were made. Perhaps, as the vortex pattern was elongated, air masses on the edge of the vortex sustained some insolation. This, together with the shorter transit times at higher altitudes, would explain how these air masses achieved less conversion of NO_x to N_2O_5 than those at lower altitudes and consequently contained high NO concentrations.

1979. The isobaric pattern of the NMC charts for the first couple of weeks of February 1979 is not as complicated as for 1978, although the overall situation was more complex, since a stratospheric warming occurred. Figures 14 and 22 show that temperatures in the Cold Lake vicinity were much warmer than normal, and the NMC charts exhibited warming maxima on January 26 and February 7 over the northern part of North America [Quiroz, 1979].

Selected NMC charts are shown in Figures 31 and 32. There was an extensive well-developed nonzonal low-pressure vortex throughout the first two weeks which did not extend as far south as Cold Lake. We have not replotted the temperature contours of the NMC charts in Figures 31 and 32, but in the region north and west of Cold Lake, the temperature contours cross the isobars at large angles. This would indicate the possibility of some vertical mixing. The circulation patterns were similar at all altitudes. The low-pressure vortex was well developed but centered in the eastern hemisphere so that Cold Lake was on the edge of the vortex for the entire period. A high-pressure area was generally centered over Alaska. From February 1 to 7 the apparent flow could have come from either the vortex or originated between 40°N and 50°N and

circled the Alaskan high to end up at Cold Lake. The latter air parcel would have reached 75°N for the lower altitudes (100–70 mbar) but only 65°N for the higher altitudes. After February 7 there was a substantial decrease in the flow over Cold Lake. At 100 and 70 mbar the high weakened and moved southwest to leave the flow over Cold Lake weak and from the outer regions of the polar vortex. At higher altitudes the high weakened but spread so that it extended almost to Cold Lake. The flow over the site then was very weak at all altitudes. Therefore the determination of whether the air originated from within the vortex could not be made from the pressure contours. Again, a detailed trajectory analysis is required.

Comparing the measurements with the previous years suggests that the air was of polar origin. The high HNO_3 distribution, the low column NO_2 , and the reduced NO indicate that a polar transit had occurred. However, the transit could have been comparatively shorter because the higher temperatures in 1979 would have increased the rate of formation of N_2O_5 from NO_x via (R4) and (R5). If the transit times were comparable, we would have expected a further decrease in NO_x in the warming situation. This could occur without dramatically changing the column NO_2 from more normal winters (1977 or 1978), because at higher temperatures and similar O_3 (cf. Figure 23), the partitioning of NO_x favors a greater fraction of NO_2 . The net result would be increased N_2O_5 mostly at the expense of NO. Our results show similar NO_2 column abundances from winter to winter. Furthermore, Figure 14 shows that at higher altitudes, above about 25 km, temperatures increased after February 4. This is also the region of maximum NO_x . The 30% increase, shown in Figure 21, in our evening column abundance of NO_2 between February 4 and 7 could reflect the temperature-induced change in NO_x partitioning. An increase of only 10°C near -45°C would be expected to increase the daytime NO_2/NO ratio by 30%.

Although we have presented only a very qualitative description of the possible influence of stratospheric dynamics, the account seems to be reasonably consistent with both our observations and the chemistry of N_2O_5 . We have also presented some evidence that in winter meridional mixing can produce unusual profiles of stratospheric species. Clearly, the northern winter stratosphere presents interesting difficulties for atmospheric modeling efforts.

CONCLUSIONS

We have presented observations made during three balloon campaigns at Cold Lake, Alberta. The vertical distributions of NO, HNO_3 , N_2O , CFM-11, and CFM-12 show substantial changes from measurements of the same species at 51°N in summer. From our wintertime observations we conclude that (1) there is more natural variation in the concentration of all reactive species than in summer, (2) the winter abundance of nitric acid is usually greater and the stratospheric layer is thicker, (3) there is less nitric oxide particularly in the 18- to 25-km region, and (4) the column abundance of NO_2 is lower in winter, but the diurnal ratio is not very different from summer values.

We have given evidence for a reduction of NO_x in winter by the production of N_2O_5 in regions of little or no insolation followed by air mass transport to Cold Lake. By using NMC

charts of upper atmospheric pressure we were able to show qualitatively that the unusual profiles resulted from air masses at different altitudes having either different origins, for example, polar or mid-latitude, or different transit times from the source to the sampling region.

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